Standard Operation Procedure for:

ANALYSIS OF ORGANONITROGEN AND ORGANOPHOSPHORUS PESTICIDES IN WATER, SOIL/SEDIMENT, AND WASTE BY GAS CHROMATOGRAPHY WITH NITROGEN-PHOSPHORUS DETECTION (GC/NPD).

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of selected organonitrogen and organophosphorus pesticides in water, sediment, and waste as listed in Table 3. Method Detection Limits and Practical Quantitation Limits yielded by this method are also provided in Table 3.

1.2. This method is in compliance with the requirements of EPA Method 614, 614.1, 619, 622, 622.1, 633 and 645 and Method 8141B for the parameters denoted as such in Table 5.1 of the laboratory's Quality Manual. EPA Methods 614, 614.1, 619 and 622 are approved test procedures of the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) and Methods 8141B is listed in the SW-846 publication under Subtitle C of the Resource Conservation and Recovery Act (RCRA). Furthermore, the NPDES and RCRA compliant tests employed by the laboratory using these methods are listed below.

Laboratory Test Name	Test Description
W-NP-AA-SF	EPA Method 614, 614.1, 619, 622, 622.1, 633 and 645 analysis, water samples, CWA (NPDES) compliant
W-PSTNP-R	EPA Method 8141B analysis, water samples, RCRA compliant
SPLP-PS-NP	EPA Method 8141B analysis, soil samples, RCRA compliant
S-PEST-NP	EPA Method 8141B analysis, soil samples, RCRA compliant
WAS-PEST-NP	EPA Method 8141B analysis, waste samples, RCRA compliant

The acceptance limits, as provided in EPA Methods 614, 614.1, 619, 622, 622.1, 633 and 645 and EPA Methods 8141B are programmed into the Target processing software and Laboratory's Information Management Systems (LIMS) and applied automatically as part of the data processing, review, and reporting procedures. Table 5 specifies the different QC performance criteria employed for CWA (NPDES) and RCRA samples.

1.3. Performance criteria for individual analytes, based on the specific EPA method, are summarized in Appendices - Table A. For parameters not listed in any of the EPA 600 methods mentioned above (references 15.11, 15.12, 15.13, 15.14, 15.15, 15.16 and 15.17) the performance criteria are based on this SOP. For parameters not mentioned in the EPA method 8141B (see ref. 15.2) the performance criteria are based on EPA 8000C (ref. 15.1), and/or this SOP.

1.4. Compound identification is supported by a dissimilar gas-chromatography column or by GC/MS.

1.5. This Standard Operation Procedure is restricted to use by an analyst experienced in the use of a Gas Chromatograph, in the interpretation of Gas Chromatograms, and in the use of appropriate computer programs. The minimum qualifications required:

- B.S. in Chemistry or Biochemistry with minimum one year of professional chemical or biochemical experience
- Knowledge of principles and practice of Gas Chromatography
- Ability to perform basic laboratory mathematics
- Knowledge of EZChrom Elite chromatography software, TARGET chromatography software, and FLDEP LIMS.

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2. SUMMARY OF THE METHOD

2.1. Water, soil/sediment, and waste samples are extracted using the appropriate procedures listed in the Preparation SOPs. The extract is analyzed using a Gas Chromatograph (GC) equipped with two capillary GC columns and two Nitrogen-Phosphorus Detectors (NPDs) to provide confirmatory analyses for all positive hits.

3. INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must routinely demonstrate to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section 9. Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 550°C for 8 hrs. Some thermally stable materials may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil. See SOP GC-003-2 for more details (reference 15.3). 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. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures described in the Prep DEP SOP GC-002.2 (reference 15.4) can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDLs listed in Table 3.
In case of observed interferences with the parameters of interest, there are several options the analyst can use to remove or alleviate the problem:

1. Process the sample extract with a validated cleanup procedure
2. Use another column type, length or diameter (if available)
3. Use another detector type (GC/MS, ECD, FPD)
4. Dilute

In case the interference cannot be removed increase the MDL to the level of the lowest value obtained in two channels.

4 DEFINITIONS

4.1 ACCURACY: The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

4.2 BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed

4.3 BIAS: The deviation due to matrix effects of the measured value (Xs - Xu) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (Xs - Xu) - K$$

where:
Xs = measured value for spiked sample,

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Xu = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100 (Xs- Xu)/ K$$

4.4 PRACTICAL QUANTITATION LIMIT (PQL): The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is generally 3 to 5 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the PQL concentration is selected as the lowest non-zero standard in the calibration curve.

4.5 FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

4.6 INTERNAL STANDARD: A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

4.7 LABORATORY FORTIFIED BLANK (LFB): A known matrix spiked with compound(s) representative of the target analytes. The LFB is analyzed exactly as a sample. This is used to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

4.8 MATRIX: The component or substrate (e.g., surface water, drinking water) which may contain the analyte of interest.

4.9 MATRIX SPIKE: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

4.10 MATRIX SPIKE DUPLICATES: A second aliquot of the same sample used for matrix spike spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.11 METHOD BLANK: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank must be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process. For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern shall not be higher than the method detection limit .

4.12 METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of seven analyses of a matrix spike containing the analyte of interest at a concentration one to five times the estimated MDL.

4.13 ORGANIC-FREE REAGENT WATER: All references to water in the method refer to water in which interference is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

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4.14 PRECISION: The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate analyses. These samples should contain concentrations of analyte above the MDL, and involve the use of matrix spikes or laboratory fortified blanks. The estimates of precision are based on the relative percent difference (RPD).

$$RPD = 100 [(X1-X2) / (X1+X2) /2]$$

where:
X1 and X2 are the two measurements

4.15 QUALITY CONTROL CHECK STANDARD (QCS): A standard solution from a source, other than normal calibration standards, that is certified and traceable. These standards are used to check the accuracy of a calibration curve.

4.16 SPIKE SOLUTION (SS): A solution of method analytes of known concentrations that is used to fortify an aliquot of laboratory reagent water or sample matrix.

4.17 STANDARD CURVE: A plot of concentrations of known analyte standards versus the ratio of the instrument response to the analyte and internal standard. Calibration standards are prepared by successively diluting a standard solution to produce working standards, which cover the working range of the instrument. Standards should be prepared at the frequency specified in section six (6) of this SOP. The calibration standards should be prepared using the same type of solvent as the final sample preparation solvent.

4.18 SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Surrogates are added to each field and QC sample prior to extraction and are used to monitor the preparation.

5 APPARATUS AND EQUIPMENT

5.1 Gas Chromatograph: Hewlett Packard 5890 Series II, Series II Plus, or Shimadzu GC-2010 capable of four steps temperature programming, with dual Nitrogen-Phosphorus detectors, dual capillary split/splitless injectors and a dual HP 7673 Automatic Sampler (or AOC-20s for Shimadzu). The GC and GC Automatic Sampler operating parameters are illustrated in Table 1 and Table 2 of the Appendixes.

5.1.1 The first analytical column is a DB-5, J & W fused silica capillary, 30 m x 0.32 mm x 0.25 um or similar column.

5.1.2 The second analytical column is a DB-17, J & W fused silica capillary, 30 m x 0.32 mm x 0.52 um or similar column.

5.1.3 Any of these columns can be assigned by the analyst as primary or confirmatory based on performance.

5.2 Data system

5.2.1 A computer system is interfaced to the Chromatograph that allows the continuous acquisition and storage on machine-readable media of all chromatographic measurements obtained throughout the duration of the chromatographic run sequence program.

5.2.2 This system currently uses the EZChrom Elite software from Agilent Technologies, Inc.(reference 15.5) for data acquisition, and Target chromatography software from Thermo Fisher Scientific, Inc (reference 15.6) for data processing and reporting of the chromatographic data.

5.2.3 For reporting data, the system currently uses the FLDEP LIMS software.

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5.3 Gases

5.3.1 Helium, UPC Grade, is used as the carrier and make up gas. The helium is passed through a oxygen and a hydrocarbon filter before it enters the GC.

5.3.2 Hydrogen, UPC Grade, is used as a combustion gas for the NPD detectors. The H_2 is passed through a hydrocarbon filter before entering the GC.

5.3.3 Air, UPC Grade is used as combustion gas for the NPD detectors. Is passed through a hydrocarbon filter prior entering the GC.

5.3.4 Gases are delivered to the instruments by the Laboratory Compressed Gas Manifold System.

6 REAGENTS AND CHEMICALS

6.1 Solvents

6.1.1 Isooctane, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.
6.1.2 Acetone, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.

6.2 Stock and Intermediate Standards

6.2.1 Individual stock standards are concentrated standards prepared from neat standards (approximately 100% purity) once a year. The concentration for all individual stock standards is 1,000 ug/mL Stock Standards mixtures are prepared from neat standards. Their concentrations are multiples of 1,000 ug/mL to match the ratios in the working standards. Standards may be prepared in the DEP lab or purchased from a certified manufacturer (ISO 9000 or EPA certified). The purchased custom made standard mixtures may have different concentrations than those prepared from neat in our lab.

6.2.2 Intermediate standard solutions are mixture or individual standards used to prepare working standards. They are prepared in our lab from stock standards by mixing / diluting with acetone or other appropriate solvents or can be purchased from a certified manufacturer (ISO 9000 or EPA certified). There are three standard mixtures used in this procedure: NPD A, NPD B, NPD C. The concentrations of the components in the intermediate standards are listed in Table 4. Standards are replaced once per year. New standards are checked vs. a second source (QC Standards), after diluting them to one of the working standard levels (usually Level 3, middle level). The criterion of acceptance is +/- 10% difference. All standard preparations and verifications have to be recorded in the Standard Preparation Tracker located in DEP LIMS. A list containing all standards with their serial numbers used in the analysis must be part of analysis documentation folder.

6.3 Working Standards Solutions (Calibration Standards)

6.3.1 Working standard solutions are a series of diluted individual or mixture standards in iso-octane: acetone (4:1). They are used for calibration and are prepared by diluting intermediate standard solutions with isooctane/acetone. Two internal standards, Triphenyl phosphate (TPP) and 5-Nitroquinoline (NQ), are added to every working standard. (See Table 4 for amount). Validity of internal standard is 13 month.

6.3.2 The concentrations for each analyte in the intermediate and diluted standards are listed in Table 4.

6.4 Spiking Solution

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6.4.1 These solutions are used when fortifying sample matrix spikes or lab fortified blanks at extraction. These fortified samples are used to verify the accuracy and precision of the sample preparation and analysis.

6.4.2 Spike solutions are prepared by diluting stock or intermediate standards with acetone. These solutions are prepared from a different source then the calibration standards, usually the same source as the one used to prepare QCS standards. Concentrations of the parameters in these solutions are listed in Table 4. Two spike solutions are made: NPDA and NPDB+C. They are used for spiking based on rotation schedule.

6.4.3 For spiking policy see DEP SOP GC-001-2, paragraph 3.5 (ref. 15.8)

6.4.4 Freshly prepared spike solutions are checked vs. valid working standards. The acceptance criterion is +/- 10 % difference.

6.5 Quality Control Check Standards (QCS) are prepared from a source (or batch) other than calibration standards, that is certified and traceable. Usually they are prepared at middle calibration level (Level 3). These standards are used to check the integrity of the calibration standards and are run and analyzed whenever an initial calibration curve is build. The acceptance criterion is +/- 15% difference.

6.6 For detailed standard preparation procedures see appendix A.

7 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples must be collected in glass containers.

7.2 All samples must be iced or refrigerated at 4 ^{o}C or less from time of collection until extraction.

7.3 All water samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

7.4 All sediment and waste samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.5 All sample extracts must be refrigerated at 4 ^{o}C or less from the time of extraction until analysis.

8 SAMPLE PREPARATION PROCEDURE

8.1 See Preparation Lab SOP GC-002.2: “EXTRACTION OF ORGANOPHOSPHORUS, ORGANONITROGEN AND ORGANOHALIDE PESTICIDES AND PCBs FROM WATER, WASTE, SEDIMENT/SOIL, PUFs AND FILTERS FOR SUBSEQUENT ANALYSIS BY GC or GC/MS TECHNIQUES “(reference 15.4).

9 GENERAL DESCRIPTION OF GC/NPD ANALYSIS

9.1 Pre-Run GC Maintenance

9.1.1 Before starting an analysis run sequence, an initial checking and maintenance of the instrument has to be performed.

9.1.2 Initial checking and maintenance of the instrument consists mainly of the following steps:

9.1.2.1 Check the detector signals to be in the accepted range

9.1.2.2 Replace the injector liner, cut 3-5 inches of the column, and replace the septum. Shimadzu GC-2010 instruments do not have replaceable gold discs.

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9.1.2.3 Run and Instrument Blank and look for instrument contamination .

9.1.2.4 In case the instrument is contaminated raise the furnace temperature to 260 ^{o}C and leave it overnight.

9.1.2.5 Re-check for instrument contamination and if needed repeat the procedure until the instrument is contamination free.

9.2 Summary of GC/NPD Analysis

9.2.1 The analysis of samples is accomplished by using two dissimilar fused silica capillary columns, usually a DB-5 and a DB-17 or similar column (usually 0.32mm ID/30m/0.25-0.50 um). For very difficult matrices, GC/MS method can be used in case of doubtful identification of positives.

9.2.2 One of the two columns, based on the best performance, is chosen by the analyst to be "primary". The "primary column" is used to report the results. Important criteria for choosing the "primary" column include:

9.2.2.1 Stable retention time windows during the entire run sequence

9.2.2.2 The best chromatography (no tailing or fronting, no impurity interference with surrogates of target components)

9.2.2.3 The best calibration curves especially for target positives

9.2.2.4 The best LCS/Matrix Spikes results

9.2.2.5 The smallest number of CCV failures

9.2.2.6 The best surrogates results

9.2.3 Analysis is accomplished in two steps: identification of positives and quantification of the positives.

9.2.4 Identification of positives requires all of the following QA/QC criteria to be meet:

9.2.4.1 Use of multipoint calibration (updated Retention Times and Response Factor).

9.2.4.2 Stable retention time windows (all calibration check standards are within the calibration windows).

9.2.4.3 Recoveries for surrogates and spikes are within the control limits.

9.2.5 The samples are analyzed in two columns for confirmation of the positives. The QC and positive reported results, are based on the "primary column" chosen by the analyst. If for some analytes QC criteria in the primary column are out of acceptable range, due to matrix interference or other problems, the results will be reported using the values found in the confirmatory column if the QC criteria are within limits.

9.2.6 A single peak target component is identified as positive if its peak is detected within its appropriate retention time window in both columns and the response exceeds the MDL. The amount of the prospective hit found in one column has to be confirmed in the other column. Criterion for the amount confirmation is equal to or less than +/-30% difference between the two columns values. In addition to the retention time, if there is other evidence that the target analyte is a positive, and the amount in two column does not match, the result will be reported based on the smallest value found in the two columns, and will be qualified as estimated (J).

9.2.7 Quantitative analysis of pesticides is accomplished by the internal standard calibration method. The calibration fit used is linear , Average Response Factor or quadratic. For building an initial calibration curve a minimum of 5 (or 3 for CWA projects, see table A) calibration levels must be used. At least six calibration levels are required for quadratic fits. The linearity of the calibration curve is defined by an RSD of 20% (RCRA projects) or 10% (CWA projects) of the

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Response Factors, or by a Correlation Coefficient bigger than 0.995. The calibration curve is additionally checked by re-fitting the lowest calibration point back to the model. The calculated amounts for each of the standard components should be within 20% of the expected values. After identification, all positives are quantified. If the quantity found is not within the calibration range the samples are diluted or re-run with a multilevel calibration curve.

9.2.8 The analyst should monitor the performance of the extraction and cleanup procedures by spiking each sample, QC sample and Method Blank with a pesticide surrogate, Nitro-m-xylene (NMX). To determine acceptance accuracy limits for the surrogate, the following procedure should be used (Reference 15.1): (1) for each sample analyzed, calculate the percent recovery of the surrogate in the sample, (2) once a minimum of seven samples of the same matrix has been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recoveries (s) of the surrogate, (3),) For a given matrix, calculate upper and lower control limit for method performance for each surrogate standard as follows:

Upper Control Limit (UCL) = p+ts
Lower Control Limit (LCL) = p -ts

Where "t" stands for student coefficient for n-1 degrees of freedom (n = no. of measurements).

9.2.9 Control Limits are supposed to be checked once per year. The statistical control limits can be replaced by statutory control limits if they are practically similar.

9.2.10 If surrogate recovery is outside control limits, the sample has to be re-run, and re-analyzed. If surrogate fails again, sample must be re-extracted and re-analyzed. If the sample exceeded the holding time for extraction and the recovery is biased high, the re-extraction is not required and the reported positive hits have to be qualified as estimated with the following comment entered in the Sample Report: "Estimated values for "parameters" are due to surrogate recovery out of control limits". If surrogates are missing or the recovery is biased low, samples should be re-extracted and re-analyzed even if they are beyond holding time.

9.2.11 Absolute Retention times (Rts) are used for the identification of targets. The absolute retention time window is assessed during initial calibration as +/- 0.03 minute of the mean RT of the analyte.

9.2.12 To demonstrate that interferences from the analytical system , reagents and glassware are under control, the analyst must analyzed one Instrument Blank (clean Isooctane) in the beginning of each run sequence and one Method Blank (extraction blank) for each extraction batch. A blank will be within acceptable range, if the concentration in that blank of any analyte of interest is below the analyte MDL and surrogate recoveries are within acceptable limits.

9.2.13 In the event a positive identification is found in both the sample(s) and the instrument blank, the instrument must be cleaned and the sample(s) rerun/reanalyzed.

9.2.14 In the event a positive identification is found in both the sample(s) and the extraction blank then the sample batch has to be re-extracted and reanalyzed. If samples passed the holding time the affected samples' results will be reported with a "V" qualifier up to ten times the amount found in the blank.

9.3 Instrument Initial Calibration

9.3.1 Quantitation of a positive hit at PQL or higher level for all target components is accomplished by using linear or quadratic fit of the calibration curve. To create an initial calibration curve using internal standard procedure, five (or 3 for CWA projects, see table A) standard calibration levels should be used. Whenever quadratic fit is applied at least six calibration standards are

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required. One of the calibration levels must be at a concentration lower than or equal to the PQL, but higher than MDL. The other concentrations should correspond to a range of concentrations for which an acceptable linear/quadratic calibration curve can be drawn. The Chromatography Software will calculate the ratio of response to the amount injected (calibration factor).

9.3.2 The system is considered to be in initial linear calibration if the Relative Standard Deviation (%RSD) of the analyte calibration factors (using peak area calculation) is less than or equal to 10% (water-CWA projects) or 20% (water-RCRA projects, soil, waste) or the Correlation Coefficient is not smaller than 0.995. If the criterion of linearity through origin is met, the average response factor can be used for quantification.

9.3.3 All initial calibration curves shall be checked vs. appropriate QCS standard, %Recovery must be within +/- 15%. If this Quality Criterion fails for parameters reported as positives, a new calibration curve must be built, samples re-run and reanalyzed. If the samples are expired, affected results must be reported as estimated.

9.4 Continuous Calibration Verification

9.4.1 After initial calibration, the detector responses for all parameters are checked on a continuing basis, at least once for every calibration mixture per run sequence (routinely every 7-10 samples) by using a continuous calibration verification (CCV). Criterion of acceptance for calibration verification is +/- 10% (CWA projects) or +/- 20% (RCRA projects) of initial calibration. The channel with acceptable CCV checks will be used to quantify and report the positives if all other quality criteria are met. If CCV fails in both channels, all samples bracketed by this standard have to be re-run for all identified positive hits exceeding PQL level. If the samples are beyond analysis holding time, all reported positive hits with failing CCV must be flagged as estimated (J).

9.4.2 If CCVs do not meet method requirements, the associated analytical results must be qualified in accordance with Lab SOP LB-027-1 (reference 15.7).

9.5 Analysis Run Sequence.

9.5.1 The analyst will set up an analysis run sequence by placing the GC vials containing the sample extracts and standards on the autosampler tray in the following order or similar:

For CWA projects:

- iso-octane blank (equipment blank)
- NPDC calibration set (Levels 1,2, 3, 4, 5,QCS)
- NPDB calibration set (Levels 1,2, 3, 4, 5,QCS)
- NPDA calibration set (Levels 1,2, 3, 4, 5,QCS)
- NPDA CCV
- NPDB CCV
- NPDC CCV
- Method Blank (MBLK)
- Laboratory Control Sample (LCS)
- Sample Matrix Spike (MS)
- Sample Matrix Spike Duplicate (MSD)
- Sample #1 to #20

For RECRA projects:

- iso-octane blank (equipment blank)
- NPDC calibration set (Levels 1,2, 3, 4, 5,QCS)
- NPDB calibration set (Levels 1,2, 3, 4, 5,QCS)

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- NPDA calibration set (Levels 1,2, 3, 4, 5,QCS)
- NPDA CCV
- NPDB CCV
- NPDC CCV
- Method Blank (MBLK)
- Laboratory Control Sample (LCS)
- Sample Matrix Spike (MS)
- Sample Matrix Spike Duplicate (MSD)
- Sample #1 to #8
- NPDA CV (not more than 12 Hrs since last CCV)
- NPDB CV
- NPDC CV
- Sample #9 to #20

9.6 Data Processing

9.6.1 Identification

9.6.1.1 Analytes are identified by matching retention times with those that are in the standard chromatographs.

9.6.2 Quantification

9.6.2.1 Positives are quantified based on their peak area. The concentration for an identified hit in the sample extract, expressed in ug/L, is based on calibration curve of the initial calibration. The Target software used to process data will do the interpolation for the sample extract. However, the analyst must ensure that all identification criteria are fulfilled and the peak area integration was correctly done. If not, the integration has to be corrected by choosing a new set of integration parameters or by manual integration (for manual integration procedure see 15.19). Additionally, Target will complete the calculation to determine the concentration of the analyte in the sample. This is done as follows:

- C_{sample} (ug/kg) = (C_x) x ($V_{extract}$) x (DF)/(W_{sample}) for sediment and waste
- C_{sample} (ug/L) = (Cx) x ($V_{extract}$) x (DF)/(V_{sample}) for water sample

  where:

- C_x -The concentration, in ug/L, of the analyte in the sample extract determined by Target.
- $V_{extract}$ -The volume of the extract, in mLs (usually 10 or 2 mLs) recorded in the preparation report.
- DF -The dilution of the sample extract recorded in the dilution report.
- W_{sample} - For sediment it is the dry weight of the sample that was extracted. For waste it is the weight of the sample taken for extraction. The weights are expressed in grams and are recorded in the preparation report.
- V_{sample} -This is the volume of the water sample taken in extraction, expressed in mLs (usually 1000 mL).

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9.7 Reporting results in FLDEP LIMS.

9.7.1 QA/QC results, MDLs, and positives are reported in the FLDEP LIMS using the Target upload program into QC Manager (Instrument: GC Pesticides : Target)(see 15.8)

9.7.2 Following data are uploaded to LIMS:

9.7.2.1 MBLK, LCS(LCSD), MS/MSD and CCVs Recoveries

9.7.2.2 LCS/LCSD or MS/MSD RPDs

9.7.2.3 Surrogate Recoveries for Samples and MBLK

9.7.2.4 Positives and MDLs for Samples

9.7.2.5 MDLs for Method Blank

9.7.3 Qualified Data are reported based on DEP SOP LB-027-1 (see 15.9)

10 QUALITY CONTROL

10.1 For QA/QC see the Lab SOP GC-001-2 (see 15.10).

10.2 Quality Control measurements, acceptance control limits and corrective actions are summarized in TABLE 5 in APPENDICES.

10.3 All data generated by a chemistry analyst are subjected to supervisory review and authorization. The supervisor is assessing the validity of data generated by assuring that all QA/QC criteria are met by checking the following review/authorization checklist:

- Check sample preparation report
  - procedure
  - surrogate and spiking solutions
  - preparation holding time
- Check project log-in folder for special requests
- Check initial calibration for linearity
- Check recoveries for QCS standards
- Check recoveries for CCV check standards
- Check surrogate recoveries
- Check accuracy and precision for LFB and Matrix Spikes
- Check internal standard recoveries
- Check retention time drift
- Check for Blanks contamination
- Check Instrument performance
- Check for positives:
  - Proper integration of the peaks (baseline)
  - Retention time confirmation
  - Amount confirmation
  - If response is within the calibration range
  - Calculations
  - Qualifiers
- Check information in the TARGET Report Header:
  - SOP #
  - Instrument ID
  - Column ID

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- Temperature program
- Evaluate the data against any field information
- Check field preservation record
- Check LIMS report:
  - Preparation and analysis dates
  - MDLs
  - Amounts reported for positives
  - Qualifiers
  - Comments
  - CV reports
  - Method Blank report
  - Surrogate report
  - For more details see DEP SOP OG-003-2, (Reference 15.11)

11 METHOD PERFORMANCE

11.1 MDLs are determined by using EPA recommended procedure (40 CFR Pt 136 Appx. B) Ref. 16.3 by analyzing at least 7 spikes in DEP well water at PQL levels. The spikes are run and analyzed in DB-5 / DB-17. The Reported MDLs are rounded up values based on the highest value measured in the two columns. The equation used to calculate the MDL is as follows:

$$MDL = S\, t_{(n-1,\ 1-a=0.99)}$$

Where: $t_{(n-1,\ 1-a=0.99)}$ is Student coeficient value for the 99% confidence level with
n=number of replicates
S=standard deviation

11.2 Instrument performance is checked by running NPD A MDL level. All parameters in this mixture should be present in the acquired chromatogram in order to accept the instrument performance

12 DATA ARCHIVAL

12.1 All raw data are retained in electronic or hard copy format. All paper formats are maintained either in the laboratory office or in a State warehouse for at least ten years. Electronic chromatographic raw data are archived by analysis file ID and instruments ID on duplicate DVDs by the Laboratory Support Section.

13 SAFETY

13.1 The toxicity or carcinogenity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Primary standards should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

13.2 Lab cloth

13.2.1 Lab coats and safety eyeglasses must be worn at all times when in any laboratory.

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13.2.2 Use gloves when handling samples, standards, or solvents, or when washing glassware.

13.3 Chemicals involved

13.3.1 Even though the toxicity or carcinogeneity of some of the reagents used in this method have not been precisely defined, each of them should be treated as a potential health hazard. From this point of view exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

13.3.2 A reference file of Material Safety Data Sheets for each reagents used, is kept in the GC room for documentation. Refer to this folder for any materials you are handling. Update this folder upon receiving new chemicals or reagents.

13.3.3 Primary standards of these toxic compounds should be prepared in a hood (See "Hood Usage"). A NIOSH/MESA approved toxic gas respirator should be worn when handling highly concentrated solutions of these compounds.

13.4 Waste disposal

13.4.1 Neat standards should be sealed and labeled.

13.4.2 All stock standards, working standards, and un-used sample extracts must be emptied into two separate waste containers for Pesticides and PCBs. The containers must be labeled properly with hazard warning labels indicating the container contents.

13.4.3 Chlorinated and non-chlorinated solvents must be stored separately and labeled properly.

13.4.4 GC vials containing, standards, and sample extracts, must be stored in two separate waste containers for Pesticides and PCBs. These containers should be labeled properly as to their contents and stored in the hood.

13.4.5 Flammable solvents must be stored in a flammables cabinet.

13.5 Hood Usage

13.5.1 Handle all sample extraction, solvent transfers, concentrations, sample preps, and cleanups in the hood at all times.

13.5.2 At any time, no more than two people can work at each hood.

13.5.3 Turn the hood on and wait for adequate airflow. If there is no flow, DO NOT USE THE HOOD!

13.6 Glassware

13.6.1 Inspect every piece of glassware to be used. Do not use any that are chipped, cracked, etched, or scratched.

13.6.2 Dispose of all unwanted, broken glassware in the blue "GLASS" box. One should discriminate between "unwanted, broken" glassware and that which is only slightly damaged and reasonably easily repairable.

13.7 For more details see DEP SOP OG-001-3 (Reference 15.12)

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14 POLLUTION PREVENTION

14.1 Standards, QC Samples, and Sample Extracts are disposed following laboratory protocol for hazardous waste disposal (see 15.12).

14.2 Contaminated samples, and all other disposed chemical wastes are sent to specialized company for incineration.

15 REFERENCES

15.1 EPA 8000C Determinative Chromatographic Separation; Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW 846; 3rd Edition, Update 4, January 3, 2008.

15.2 EPA 8141B Organophosphorus Compounds by Gas Chromatography, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW 846; 3rd Edition, Update 4, January 3, 2008.

15.3 DEP SOP GC-003-2, Glassware Cleaning Protocol in the Organic Preparations Laboratory

15.4 DEP SOP GC-002-2, Extraction of Organophosphorus, Organonitrogen, Organohalide, and PCBs from Water, Wastes, Sediment, PUFs, and Filters for Subsequent Analysis by GC or GC/MS Techniques..

15.5 DEP SOP CM-015-1, Ezchrom Elite Client/Server Chromatography Data System.

15.6 DEP SOP CM-016-1, Target Chromatography Software.

15.7 DEP SOP LB-027-1, Standard Operating Procedure for Reporting Qualified Data.

15.8 DEP SOP GC-001-2, Quality Assurance/Quality Control in the GC Pesticides Laboratory.

15.9 DEP SOP OG-003-2, Data Review and Authorization Checklist for GC Pesticides and Associated Sample Preparation.

15.10 DEP SOP OG-001-3; Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories)

15.11 EPA 614 The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.

15.12 EPA 614.1 The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.

15.13 EPA 619 The Determination of Triazine Pesticides in Municipal and Industrial Wastewater,

15.14 EPA 622 The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.

15.15 EPA 622.1 The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater.

15.16 EPA 633 The Determination of Organonitrogen Pesticides in Municipal and Industrial Wastewater.

15.17 EPA 645 The Determination of Certain Amine Pesticides and Lethane in Municipal and Industrial Wastewater

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16 APPENDICES

Table A M**ethods performance criteria for water test methods used in DEP SOP GC-012-3.**

Parameter	Method	Performance requirements				Initial Calibration	
		CCV %Rec.	Surrogates %Rec.	LCS/MS %Rec.	LCS/MS %RPD	Calibration levels	Linearity criterion
ACETOCHLOR	GC-012-3	+/-10	Lab Stat	60-130	</=30	3	10% rsd
	GC-012-3	+/-20		60-130	</=30	5	20%rsd
ALACHLOR	EPA 645	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
AMETRYN	EPA 619	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
ATRAZINE	EPA 619	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
ATRAZINE DESETHYL	GC-012-3	+/-10	Lab Stat	48-108	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	48-108	</= 30	5	20% rsd
ATRAZINE DESISOPROPYL	GC-012-3	+/-10	Lab Stat	21-50	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	21-50	</= 30	5	20% rsd
AZINPHOS METHYL	EPA 614	+/-10	Lab Stat	78-144	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	78-144	</= 30	5	20% rsd
BROMACIL	EPA 633	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
BUTYLATE	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
CHLORPYRIPHOS ETHYL	EPA 622	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
CHLORPYRIPHOS METHYL	EPA 622	+/-10	Lab Stat	47-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	47-130	</= 30	5	20% rsd
CYANAZINE	GC-012-3	+/-10	Lab Stat	80-157	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	80-157	</= 30	5	20% rsd
DEMETON	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
DIAZINON	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
DISULFOTON	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
EPTC	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
ETHION	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
ETHOPROP	EPA 622	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
FENAMIPHOS	GC-012-3	+/-10	Lab Stat	86-148	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	86-148	</= 30	5	20% rsd
FIPRONIL	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
FONOFOS	EPA 622.1	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
HEXAZINONE	EPA 633	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
MALATHION	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
METALAXYL	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
METOLACHLOR	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
METRIBUZIN	EPA 633	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
MEVINPHOS	EPA 622	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
MOLINATE	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd

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Parameter	Method	Performance requirements				Initial Calibration	
		CCV %Rec.	Surrogates %Rec.	LCS/MS %Rec.	LCS/MS %RPD	Calibration levels	Linearity criterion
NALED	EPA 622	+/-10	Lab Stat	49-190	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	49-190	</= 30	5	20% rsd
NORFLURAZON	EPA 645	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
PARATHION ETHYL	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
PARATHION METHYL	EPA 614	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
PENDIMETHALIN	GC-012-3	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
PHORATE	EPA 622	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
PROMETON	EPA 619	+/-10	Lab Stat	81-152	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	81-152	</= 30	5	20% rsd
PROMETRYN	EPA 619	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	GC-012-3	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
SIMAZINE	EPA 619	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd
TERBUFOS	EPA 614.1	+/-10	Lab Stat	60-130	</= 30	3	10% rsd
	EPA 8141B	+/-20	Lab Stat	60-130	</= 30	5	20% rsd

TABLE 1: OPERATING PARAMETERS FOR GC/NPD ANALYSIS (METHOD NPDCV35)

GC PARAMETER	SETTING	GC PARAMETER	SETTING
Temperature 1	80° C	Injector Temperature	220° C
Time 1	1 minute	Detector Temperature	280° C
Ramp 1	9° C per minute	Carrier Gas	Helium
Temperature 2	180° C	Column Head Pressure	23.8 psi, 18 psi
Time 2	2.0 minutes	Column Flow Rate	5.83, 3.93 mL per minute
Ramp 2	2.0° C per minute	Septum Purge Flow Rate	3.0 mL per minute
Temperature 3	195° C	Make up Gas	Helium
Time 3	0 minute	Make up Gas Flow Rate	20 mL per minute
Ramp 3	10.0° C per minute	Hydrogen Gas Flow Rate	1.0 mL per minute
Temperature 4	275° C	Air Flow Rate	150 mL per minute
Time 4	5.39 minutes	Injection Mode	Splitless for 1 minute
		Injection Volume	1.0 uL
		control mode	constant velocity

TABLE 2:GC AUTOSAMPLER OPERATING PARAMETERS FOR GC/NPD ANALYSIS (OPTION-SAMPLER-ALLOC-MODE4)

Autosampler Parameter	Setting	Autosampler Parameter	Setting
Inj/Bottle	1	Volume	1 uL
First Bottle	1	# of pre-solvent washes	6 (Acetone)
Last Bottle	150	# of solvent washes	6 (Iso-Octane)
# of Sample washes	2	Priority Sample (1=Yes)	No

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# of Pumps	6	Capillary On-Column (1=Yes)	No
Viscosity	0.2	Syringe	10 uL

TABLE 3: ESTIMATED RETENTION TIMES AND METHOD DETECTION LIMITS

Components			Water	Water	Water	Water	Soil	Soil	Waste	Waste
	RT DB-5	RT DB -17	MDL AA	PQL AA	MDL	PQL	MDL	PQL	MDL	PQL
	minute	minute	ug/L	Ug/L	ug/L	ug/L	ug/kg	ug/kg	ug/kg	ug/kg
Acetochlor	14.2	15.6	0.060	0.24	0.30	1.2				
Alachlor	25.6	17.4	0.060	0.24	0.30	1.2	12	48	360	1400
Ametryn	25.6	18.8	0.010	0.040	0.05	0.20	1.7	6.8	50	200
Atrazine	20.0	14.7	0.010	0.040	0.05	0.20	1.7	6.8	50	200
Atrazine Desethyl	10.22	12.22	0.010	0.040	0.05	0. 20	3.3	13	100	400
Atrazine Desisopropyl	10.07	12.38	0.010	0.040	0.05	0. 20				
Azinphos Methyl	38.9	35.9	0.020	0.080	0.10	0.40	5	20	150	600
Bromacil	26.9	22.2	0.040	0.16	0.20	0.80	10	40	300	1200
Butylate	12.5	8	0.020	0.080	0.10	0.40	4	16	120	480
Chlorpyrifos Ethyl	28.2	19.7	0.010	0.040	0.05	0.20	1.7	6.8	50	200
Chlorpyrifos Methyl	25.1	17.8	0.010	0.040	0.05	0.20	1.7	6.8	50	200
Cyanazine	16.3	21.7	0.020	0.080	0.10	0.40				
Demeton	12.2	12.4	0.024	0.96	0.12	0.48	2.0	8.0	60	240
Diazinon	21.7	14.7	0.010	0.040	0.05	0.20	1.7	6.8	50	200
Disulfoton	22.1	15.2	0.005	0.020	0.025	0.10	0.83	3.3	25	100
EPTC	7.1	7.1	0.020	0.080	0.10	0.40				
Ethion	34.2	29.3	0.010	0.040	0.050	0.20	1.7	6.8	50	200
Ethoprop	16.8	12.2	0.005	0.020	0.025	0.10	0.83	3.3	25	100
Fenamiphos	31.8	26.8	0.030	0.12	0.15	0.60	3.3	13	100	400
Fipronil	18.4	18.7	0.060	0.24	0.30	1.2				
Fonofos	21.4	15.1	0.010	0.040	0.050	0.20	0.83	3.3	25	100
Hexazinone	35.8	33.4	0.030	0.120	0.15	0.60	5.0	20	150	600
Malathion	27.5	20.4	0.010	0.040	0.050	0.20	1.7	6.8	50	200
Metalaxyl	25.9	19.1	0.040	0.16	0.20	0.80	6.7	27	200	800
Methamidophos	8.9	10.4					6.7	27	200	800
Metolachlor	28.0	19.1	0.060	0.24	0.30	1.2	10	40	300	1200
Metribuzin	24.4	19.1	0.020	0.080	0.10	0.40	3.3	13	100	400
Mevinphos	12.4	9.9	0.010	0.040	0.050	0.20	1.7	6.8	50	200
Molinate	9.4	10.5	0.020	0.080	0.10	0.40				
Monocrotophos	17.6	21.3					2.0	8.0	60	240
Naled	9.5	6.7	0.040	0.16	0.20	0.80	6.7	27	200	800
Norflurazon	35.2	31.7	0.030	0.120	0.15	0.60	5.0	20	150	600
Parathion Ethyl	28.2	20.1	0.020	0.080	0.10	0.40	1.7	6.8	50	200
Parathion Methyl	25.0	18.4	0.010	0.040	0.050	0.20	1.7	6.8	50	200
Pendimethalin	17.6	19.6	0.040	0.16	0.20	0.80				
Phorate	18.6	13.1	0.005	0.020	0.025	0.10	0.83	3.3	25	100
Prometon	11.22	12.64	0.020	0.080	0.10	0.40	3.3	13	100	400
Prometryn	25.8	18.5	0.020	0.080	0.10	0.40	3.3	13	100	400
Simazine	19.7	14.9	0.010	0.040	0.050	0.20	1.7	6.8	50	200
Terbufos	21.1	14.0	0.005	0.020	0.025	0.10	0.83	3.3	25	100

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TABLE 4: STANDARD CONCENTRATION LEVELS AND INTERNAL STANDARD ASSOCIATIONS FOR NPD A,B,C, MIXTURES

Parameter		Standard Solution (ug/L)							Spike Solution (ug/L)
	ISTD	Intermediate	Dil. 1	Dil. 2	Dil. 3	Dil. 4	Dil. 5	Dil 6	
NPD A MIX									
Ametryn	NQ	5000	500	200	100	50	35	20	1000
Atrazine	NQ	5000	500	200	100	50	35	20	1000
Atrazine Desethyl	NQ	5000	500	200	100	50	35	20	1000
Chlorpyrifos Ethyl	NQ	5000	500	200	100	50	35	20	1000
Chlorpyrifos Methyl	NQ	5000	500	200	100	50	35	20	1000
Disulfoton	NQ	2500	250	100	500	25	17.5	10	500
EPTC	NQ	20000	2000	800	400	200	140	80	4000
Ethion	TPP	5000	500	200	100	50	35	20	1000
Ethoprop	NQ	2500	250	100	50	25	17.5	10	500
Fipronil	NQ	10000	1000	400	200	100	70	40	2000
Hexazinone	TPP	15000	1500	600	300	150	105	60	3000
Malathion	NQ	5000	500	200	100	50	35	20	1000
Metribuzin	NQ	10000	1000	400	200	100	70	40	2000
Mevinphos	NQ	5000	500	200	100	50	35	20	1000
Molinate	NQ	20000	2000	800	400	200	140	80	4000
Norflurazon	TPP	15000	1500	600	300	150	105	60	3000
Pendimethalin	NQ	10000	1000	400	200	100	70	40	2000
Prometryn	NQ	10000	1000	400	200	100	70	40	2000
Phorate	NQ	2500	250	100	50	25	17.5	10	500
Simazine	NQ	5000	500	200	100	50	35	20	1000
Terbufos	NQ	2500	250	100	50	25	17.5	10	500
NPD B MIX									
Acetochlor	NQ	30000	3000	1200	600	300	210	120	6000
Azinphos Methyl	TPP	10000	1000	400	200	100	70	40	2000
Cyanazine	NQ	20000	2000	800	400	200	140	80	4000
Diazinon	NQ	5000	500	200	100	50	35	20	1000
Metalaxyl	NQ	20000	2000	800	400	200	140	80	4000
Methamidophos	NQ	10000	1000	400	200	100	70	40	2000
Monocrotophos	NQ	5000	500	200	100	50	35	20	1000
Naled	NQ	20000	2000	800	400	200	140	80	4000
Prometon	NQ	10000	1000	400	200	100	70	40	2000
NPD C MIX									
Alachlor	NQ	30000	3000	1200	600	300	210	120	6000
Atrazine Desisopropyl	NQ	5000	500	200	100	50	35	20	1000
Diazinon	NQ	5000	500	200	100	50	35	20	1000

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Parameter		Standard Solution (ug/L)							Spike Solution (ug/L)
	ISTD	Intermediate	Dil. 1	Dil. 2	Dil. 3	Dil. 4	Dil. 5	Dil 6	
Bromacil	NQ	20000	2000	800	400	200	140	80	4000
Butylate	NQ	10000	1000	400	200	100	70	40	2000
Demeton	NQ	5000	500	200	100	50	35	20	1000
Fonofos	NQ	2500	250	100	50	25	17.5	10	500
Fenamiphos	TPP	10000	1000	400	200	100	70	40	2000
Metolachlor	NQ	30000	3000	1200	600	300	210	120	6000
Parathion Ethyl	NQ	5000	500	200	100	50	35	20	1000
Parathion Methyl	NQ	5000	500	200	100	50	35	20	1000

* Add 5 uL of 50 ug/mL TPP/ 100ug/mL NQ ISTD mix to every 1.0 mL of sample or standard.
NQ: 5- Nitroquinoline
TPP: Triphenyl phosphate

TABLE 5: QC MEASUREMENTS AND ACCEPTANCE CRITERIA

#	QC MEASUREMENT	ACCEPTANCE CRITERION		CORRECTIVE ACTION
		CWA (NPDES)	RCRA	
1	LFB/Matrix spike* recoveries	60-130 %	60-130 % (s)	Reanalyze/Re-extract/Flag/Comment
	Naled	49-190%	45-192% (s)	
	Atrazine Desisopropyl	21-50%		
	Atrazine Desethyl	48-108%		
	Azinphos Methyl	78-144%	76-138% (s)	
	Cyanazine	80-157%		
	Fenamiphos	86-148%	65-151% (s)	
	Prometon	81-152%	76-142% (s)	
	Chlorpyrifos Methyl	47-130%		
	Monocrotophos		30-145% (s)	
	Methamidophos		14-131% (s)	
	LFB/MS precision	=/< 30 %	=/< 30 %	
3	Cal. Verification	+/- 10%	+/- 20 %	Re-run and recalibrate/Flag/Comment
4	Surrogate recovery NMX	54-108%	33-118% (soil)	Reanalyze/Re-extract/Flag/Comment
5	Internal standard recovery	50%-200%	50%-200%	Reanalyze/Flag/Comment

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#	QC MEASUREMENT	ACCEPTANCE CRITERION		CORRECTIVE ACTION
5	QCS verification	+/- 15%	+/- 15%	Re-run and recalibrate/Flag/Comment
6	Instrument performance	Annual MDL verification For more details see DEP SOP GC-001-2 (Reference 15.15)	Annual MDL verification For more details see DEP SOP GC-001-2 (Reference 15.15	Maintain and re-run
7	Calibration Levels Calibration Fit Acceptance criterion	3 levels linear 10%RSD	5 levels Linear, 6 levels quadratic 20% RSD 0.995 CC	Use appropriate cal fit / Re-run/ Recalibrate/Flag/Comment
8	Lowest calibration point re-fitting	+/- 20% of expe value	+/- 20% of expe value	Use appropriate cal fit/Re-run/ Recalibrate/Flag/Comment

- * Statutory limits are used for assessing LFB/matrix spike recoveries. The limits are verified annually based on statistical data. Statistical limits are those analytes that differ significantly from the statutory limits. For water matrices the LFB and surrogate recovery limits are the same for CWA and RCRA samples and are listed only in the CWA column.

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Appendix A
Preparation of NPD standards

Stock solutions usually come in 1mL glass vials. Take the vials out of the freezer at least 30min before preparation. Open vials and transfer the entire solution into 10mL centrifuge vials (using Pasteur pipettes). Record the transfer date and keep the vial label.

The Intermediate Standard is prepared by diluting the Stock solution. The Working Level Standards are prepared by diluting the Intermediate Standard.

Surrogate:

The individual surrogate stock solution is prepared from purchased neat material.

Neat	Components	Source
1000mg	NMX	Chem Service

Individual Stock solution:
Solvent: Acetone

Component	Neat added mg	Stock V_f mL	Conc. Stock ug/mL
NMX	50	50	1000

Surrogate spike solution (Mix):
Solvent: Acetone

Component	Amount Stock added mL	Dilution Factor	Surr. spike V_f mL	conc.ug/mL
TMX*	3.125	80	250 ml	2.5
DCB**	6.250	40		5
NMX***	12.5	20		50

*Tetrachloro-M-Xylene. (ECD surrogate also present in the mix)
**Decachlorobiphenyl. (ECD surrogate also present in the mix)
***Nitro-M-Xylene.

Internal standard:

The individual internal standard stock solution is prepared from purchased neat material.

Neat	Components	Source
100mg	TPP****	Chem Service
100 mg	NQ*****	Acros Organics

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Individual Stock solution:
Solvent: Acetone

Component	Neat added mg	Stock V_f mL	Conc. Stock ug/mL
TPP	50	50	1000
NQ	100		2000

Internal standard intermediate solution
Solvent: Acetone

Component	Amount Stock added (mL)	Dilution Factor	Surr. spike V_f mL	conc.ug/mL
TPP/NQ	10	20	200	50/100

Isooctane+Internal standard solution
Solvent: isooctane

Component	Amount spike added (mL)	Dilution Factor	Surr. spike V_f mL	conc.ug/L
TPP/NQ	1	200	200	250/500

**** Triphenyl phosphate
***** 5-Nitroquinoline

NPDA Custom Mix:

Solvent: ethyl acetate

Stock conc. ug/mL	Components	Source
62.5	Disulfoton, Ethoprop, Phorate, Terbufos	1.AccuStandard 2.Crescent Chem.
125	Ametryn, Atrazine, Atrazine Desethyl, Chlorpyrifos Ethyl, Chlorpyrifos Methyl, Ethion, , Simazine, , Malathion, Mevinphos,	
250	, Metribuzin, , Prometryn, EPTC, Molinate, Fipronil, Pendimethalin	
375	Norflurazon, Hexazinone	

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Intermediate NPDA Standard Solution:

Amount **Accustandard NPDA** Stock added (**mL)**	Dilution Factor	**INT** in acetone	
		V_f mL	conc. ug/mL
2	25	**50**	2.5-15
Amount **NMX** Stock added (mL)			
1.25	40		25

Amount **Crescent Chemical NPDA** Stock added (mL)	Dilution Factor	**INT QCS** in acetone	
		V_f mL	conc. ug/mL
1	25	25	2.5-15

NPDA Working Level Standards:
Solvent: ISO-8:ACETONE 4:1 V/V

	V_f mL	Amount NPDA INT added (mL)	Amount INTERNAL STD SPIKE added (mL)	Dilution Factor	Conc. (ug/L)
L1	100	10	0.5	10	250-1500
L2	100	4	0.5	25	100-600
L3	200	4	1.0	50	50-300
L4	100	1	0.5	100	25-150
L5	100	0.7	0.5	175	17.5-105
L6	100	0.4	0.5	250	10-60
MDL	100	0.1	0.5	1000	2.5-15
L3 QCS	100	2	0.5	100	50-300
SPK	100	20		5	500-3000

* NPDA QCS INT added, spike solution in acetone.

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NPDB Custom Mix:

Solvent: Acetone

Stock conc. ug/mL	Components	Source
		1.Accustandard 2.Crescent Chemical
150	Monocrotophos	
250	Azinphos Methyl, , Prometon, Methamidophos, , Cyanazine	
500	Metalaxyl, , Naled	
750	Acetochlor	

Intermediate NPDB Standard Solution:

Amount **AccuStandard NPDB** Stock added (**mL)**	Dilution Factor	**INT** in Acetone	
		V_f mL	conc. ug/mL
1	25	25	5-20

Amount **Crescent Chem. NPDB** Stock added (**mL)**	Dilution Factor	**QCS INT** in Acetone	
		V_f mL	conc. ug/mL
1	25	25	5-20

NPDB Working Level Standards:
Solvent: ISO-8:ACETONE 4:1 V/V

	V_f mL	**Amount NPDB INT added (mL)**	**Amount INTERNAL STD SPIKE added (mL)**	**Dilution Factor**	**Conc. ug/L**
L1	100	10	0.5	10	500-2000
L2	100	4	0.5	25	200-800
L3	200	4	1	50	100-400
L4	100	1	0.5	100	50-200
L5	100	0.7	0.5	175	35-140
L6	100	0.4	0.5	250	20-80
L3 QCS*	100	1	0.5	100	100-400

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NPDC Custom Mix:

Solvent: Acetone

Stock conc. ug/mL	Components	Source
62.5	Fonofos	1.AccuStandard 2.Crescent Chemical
125	Atrazine Desisopropyl, Parathion Ethyl, Parathion Methyl, Diazinon	
150	Demeton	
250	Butylate, Fenamiphos,	
500	Bromacil	
750	Alachlor, Metolachlor	

Intermediate NPDC Standard Solution:

Amount **AccuStandard NPDB** Stock added (**mL)**	Dilution Factor	**INT** in Acetone	
		V_f mL	conc. ug/mL
1	25	25	2.5 - 30

Amount **Crescent Chem. NPDB** Stock added (**mL)**	Dilution Factor	**QCS INT** in Acetone	
		V_f mL	conc. ug/mL
1	25	25	2.5 - 30

NPDC Working Level Standards:
Solvent: ISO-8:ACETONE 4:1 V/V

	V_f (mL)	**Amount NPDC INT added (mL)**	**Amount INTERNAL STD SPIKE added (mL)**	**Dilution Factor**	**Conc. (ug/L)**
L1	100	10	0.5	10	250-3000
L2	100	4	0.5	25	100-1200
L3	200	4	1	50	50-600
L4	100	1	0.5	100	25-300
L5	100	0.70	0.5	175	17.5-210
L6	100	0.4	0.5	250	10-120
L3 QCS*	100	1	0.5	100	50-600

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Preparation of NPDB+NPDC spike:

	V_f (mL)	Amount NPDB QCS INT added (mL)	Amount NPDC QCS INT added (mL)	Dilution Factor	Conc. (ug/L)
NPDB+NPDC spike (in Acetone)	100	20	20	5	500-6000

APPENDIX B

Replacing and recoating NPD beads in Shimadzu GC-2010

REPLACING NPD BEADS IN SHIMADZU GC 2010

1) Lower the detector temperature to 25C. Lower the oven temperature to 25C.
2) Turn FTD control OFF (top line).
3) Press SYSTEM and STOP GC.
4) Turn off the main power switch.
5) Loosen the short and long screws on the FTD and remove the cover.
6) Remove the collector by turning it manually.
7) Install the new collector by manually screwing it all the way down for best N sensitivity.
8) Reinstall the cover and turn on the GC. Turn the FTD control ON. Raise the temperatures to normal operating conditions. Raise the detector temperature to 310 C for 1 hr and then lower to 280 C.
9) Leave the bead overnight to equilibrate. Do not turn the power controller ON.
10) On the next day set the current to a value about 0.5 pA higher than normal operating conditions for the bead. Set time to 120 min and turn the power controller ON.
11) When the adjustment process is finished turn the power controller OFF and wait 1 hr.
12) Set current to 1.2 pA and adjusting time to 4320 min (72 hrs). Start conditioning the bead. This procedure is typically done over a weekend. While even longer conditioning times should not hurt, shorter may result in unsatisfactory results.
13) Turn power controller OFF and wait 1 hr.
14) Set current to normal operating value (currently about 2.0 pA) and condition the bead for 120 minutes before running samples.

RECOATING NPD BEADS IN SHIMADZU GC 2010

1) Lower the detector temperature to 25C. Lower the oven temperature to 25C.
2) Remove the detector cover and two (the left and the middle) screws on the detector upper surface.
3) Remove the detector part from the nozzle base and turn it upside down.
4) In DET screen change MODE from CURRENT to VOLTAGE.
5) Retighten the side screws.
6) Set the Voltage to around 60-70%, that is ABOVE the value needed for the ignition. Turn on the power controller The bead should be now bright orange.

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7) Using tweezers and watching the process through a magnifying glass keep the alkali source rod touching the coil on the outside so the salt melts and spreads all over the coil. The bright orange color should not be quenched by this process.
8) Mount the detector to the nozzle base and replace the two top surface screws.
9) Wait 5-10 min.
10) Turn of the power controller and change the MODE back to CURRENT.
11) Reinstall the detector cover and wait at least 1 hour.
12) Set the current to a value about 0.5 pA higher than normal operating conditions for the bead. Set time to 120 min and turn the power controller ON.
13) When the adjustment process is finished turn the power controller OFF and wait 1 hr.
14) Set current to 1.2 pA and adjusting time to 4320 min (72 hrs). Start conditioning the bead. This procedure is typically done over a weekend. While even longer conditioning times should not hurt, shorter may result in unsatisfactory results.
15) Turn power controller to OFF and wait 1 hr.
16) Set current to normal operating value (currently about 2.0 pA) and condition the bead for 120 minutes before running samples.

    It appears that FTD beads can be successfully recoated once, sometimes twice. The third attempt usually doesn't produce satisfactory results. Due to the tediousness of the current procedure the third time is probably not worth trying.

APPENDIX OF SIGNIFICANT CHANGES

10/25/2012	Nine new analytes were added to the SOP for the upcoming Pesticides Monitoring Project
10/16/2013	Requirement for six levels for quadratic calibration have been added. The statistical limits formula for surrogate recoveries have been updated. Updated standard preparations. Language describing differences between CWA (NPDES) and RCRA methods has been modified.
10/07/2014	Some standard concentrations changed. Removal of Carbofuran and Carbaryl due to their removal from the standard mixes. Those analytes were never reproted to customers.
09/28/2015	Updated QC limits table; updated standard concentartions table and added Appendix B "Replacing and recoating NPD beads in Shimadzu GC-2010".
01/06/2016	Updated QC limits table; updated standard mixes for components and concentrations.

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