**Standard Operation Procedure for:**

# ANALYSIS OF ORGANONITROGEN AND ORGANOPHOSPHORUS PESTICIDES IN WATER 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, 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 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). The NPDES 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 |

The acceptance limits, as provided in EPA Methods 614, 614.1, 619, 622, 622.1, 633 and 645 are programmed into the Masshunter 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)

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.

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, Masshunter chromatography software, and FLDEP LIMS.

## 2. SUMMARY OF THE METHOD

2.1. Water 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


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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,
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.


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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.

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.


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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: Shimadzu GC-2010 capable of four steps temperature programming, with dual Nitrogen-Phosphorus detectors, dual capillary split/splitless injectors and a dual Automatic Sampler (AOC-20s). 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.

This system currently uses the EZChrom Elite software from Agilent Technologies, Inc.(reference 15.5) for data acquisition, and Masshunter chromatography software from Agilent Technologies, Inc for data processing and reporting of the chromatographic data. The EZchrom data are automatically exported to The Masshunter processing computer as .CDF files. Those are then converted using the Agilent's GCMS Translator, and selecting the AIA option ("translate ANDI/CDF files").

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

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.


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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 two standard mixtures used in this procedure: NPD A, and NPD B. 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 4, 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). The internal standard is valid for 13 months.

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

6.4 Spiking Solution

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. 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)


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6.4.4 Freshly prepared spike solutions are checked vs. valid working standards. The acceptance criterion is +/- 15 % 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 4). 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 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 6 $^{o}$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 6 $^{o}$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.

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.

9.1.3 Troubleshooting following runs producing poor data quality.

If root cause analysis of runs with poor data quality indicates an instrument performance problem then more detailed troubleshooting may be needed to address the issue. The following are the steps that may need to be taken to restore the performance of an NPD instrument:


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9.1.3.1. If after the second column trimming the chromatographic performance is not restored the column may need to be replaced.

9.1.3.2. Clean or replace the autosampler syringe. Surprising numbers of chromatographic problems are caused by dirty autosampler syringes.

9.1.3.3. Clean and bake the injection port.
9.1.3.4. Check inlet and detector assemblies for leaks using electronic leak detector. Fix any leaks discovered.

9.1.3.5. Replace the detector- side jet.

9.1.3.6. If excessive noise is observed in the baseline, check the gas lines for leaks and verify the purity of gases used (helium, nitrogen). Replace the gas lines filters, if needed.

9.1.3.7. If the detector bead appears to be a problem, replace or re-coat the bead (see appendix B_

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 reported QC and positive 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.


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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 both columns do 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 Response Factors, or by a Correlation Coefficient bigger than 0.995. Do not use the "include origin" option for the calibration fits. The calibration curve is additionally checked by re-fitting all calibration points back to the model. The calculated amounts for each of the standard components should be within 20% of the expected values. Removal of internal calibration points is prohibited, unless the entire level is removed (all analytes in the mix) for clearly identified reason like bad injection. Lowest or highest points may be removed for specific analytes, provided that proper consideration is given to such an action. That includes a possible change of PQL and calibration fit (quadratic fit is not allowed with five points). 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 checked and updated 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 the surrogate fails again, the sample must be re-extracted and re-analyzed. If the sample exceeded the holding time for extraction and the recovery is biased high, 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 analyze one Instrument Blank (clean Isooctane) in the beginning of


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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 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).

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% or the Correlation Coefficient is not smaller than 0.995. If a higher order curve is to be used the correlation coefficient has to be at least 0.995. When new calibration is inspected linear fit is usually tried first, followed by average response factor (%RSD which is equivalent to weighted linear forced through origin), then followed by quadratic fit and finally higher order curves. Do not use the "include" origin option in the Masshunter software. "Ignore" origin is preferable to "force" through origin in most cases. Forcing the curve through origin is acceptable whenever ignoring origin produces nonsensical results for small peaks close to MDL (like negative values). When calibration curve fit is selected in the Masshunter software the % calibration drift has to be monitored in order to have all the calibration levels within 70-130% of the expected value. Special care has to be taken to carefully fit the curves at the lower end of the calibration range where the vast majority of problems occur. All calibration curves should be weighted curves (1/x or 1/x2); do not use equal weighing. It is permissible to remove individual analyte calibration levels from either the lowest and/or highest levels of the curve (the PQL may have to be adjusted). Removal of interior levels is forbidden. An entire single standard calibration level may be removed from the interior of the curve whenever the standard was not correctly injected or a wrong standard was injected. If more than 10% of the total number of analytes fail the calibration fit criteria or more than 20% of analytes fail the % calibration drift criteria, then the instrument system must be corrected. Some possible problems include standard mixture degradation, injection port inlet contamination, analytical column contamination, and active sites in the column or chromatographic system.

9.3.2 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


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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)
- NPDB calibration set (Levels 1,2, 3, 4, 5,6, QCS )
- NPDA calibration set (Levels 1,2, 3, 4, 5, 6 QCS )
- NPDA CCV
- NPDB CCV
- Method Blank (MBLK)
- Laboratory Control Sample (LCS)
- Sample Matrix Spike (MS)
- Sample Matrix Spike Duplicate (MSD)
- Sample #1 to #20

For RECRA projects (soils, wastes and SPLP samples):

- iso-octane blank (equipment blank)
- NPDB calibration set (Levels* 1,2, 3, 4, 5, 6, QCS )
- NPDA calibration set (Levels 1,2, 3, 4, 5, 6, QCS )
- NPDA CCV
- NPDB 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
- Sample #9 to #20

* calibration levels for NPDB mix are entered as 7,8,9,10,11,12 in Masshunter software to avoid overwriting response factors by coeluting peaks from the other mix.

9.6 Data Processing

9.6.1 Identification


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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 Masshunter 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, QC Manager program will complete the calculation to determine the concentration of the analyte in the sample. This is done as follows:

- $C_{sample}$ (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 Masshunter.

- $V_{extract}$ -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.

- $V_{sample}$ -This is the volume of the water sample taken in extraction, expressed in mLs (usually 1000 mL).

9.7 Reporting results in FLDEP LIMS.

9.7.1 QA/QC results, MDLs, and positives are reported in the FLDEP LIMS using the the QC Manager program (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.


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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 Masshunter Report Header:
  - SOP #
  - Instrument ID
  - Column ID
  - 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 or below PQL levels. The spikes are extracted in, at least, three different batches on, at least, three different days and spread between all the instruments used for this analysis. The spikes are run and analyzed in DB-5 / DB- 17. The Reported MDLs are rounded up values


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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

11.3 MDLs are verified quarterly and recalculated annually. At least two spikes are run in each instrument per quarter in which samples are analyzed. The spikes are prepared at concentration between MDL and PQL and it is also considered a PQL verification. The MDLs are recalculated annually (at least) based on the last 24 months of data. Both spikes and blanks are used in calculations. If the calculated MDL is within a factor of 2 of the current MDL, the current MDL may be kept unchanged. Otherwise, the MDL has to be changed to the new calculated value. MDL/PQL verification spikes are reported to LIMS as QC type SRM. The LIMS statistics module is used for the annual re-calculation of MDLs.

## 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 carcinogenicity 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.

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 carcinogenicity 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 reagent 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.


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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)

## 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


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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 | Initial Calibration | | | | |
|---|---|---|---|---|---|---|
| | | CCV %Rec. | Surrogate, LCS, MS %Rec. | LCS/MS %RPD | Calibration levels | Linearity criterion |
| ALACHLOR | EPA 645 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| AMETRYN | EPA 619 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| ATRAZINE | EPA 619 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| ATRAZINE DESETHYL | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| ATRAZINE DESISOPROPYL | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| AZINPHOS METHYL | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| BROMACIL | EPA 633 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| BUTYLATE | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| CHLORPYRIPHOS ETHYL | EPA 622 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| CHLORPYRIPHOS METHYL | EPA 622 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| DEMETON | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| DIAZINON | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| DISULFOTON | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| ETHION | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| ETHOPROP | EPA 622 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| FENAMIPHOS | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| FONOFOS | EPA 622.1 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| HEXAZINONE | EPA 633 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| MALATHION | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| METALAXYL | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| METOLACHLOR | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| METRIBUZIN | EPA 633 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| MEVINPHOS | EPA 622 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| NALED | EPA 622 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| NORFLURAZON | EPA 645 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| PARATHION ETHYL | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| PARATHION METHYL | EPA 614 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| PENDIMETHALIN | GC-012-3 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| PHORATE | EPA 622 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |


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| Parameter | Method | Initial Calibration | | | | |
|---|---|---|---|---|---|---|
| | | CCV %Rec. | Surrogate, LCS, MS %Rec. | LCS/MS %RPD | Calibration levels | Linearity criterion |
| PROMETON | EPA 619 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| PROMETRYN | EPA 619 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| SIMAZINE | EPA 619 | +/-10 | Lab Stat | </= 30 | 3 | 10% rsd |
| | | | | | | |
| TERBUFOS | EPA 614.1 | +/-10 | Lab Stat | </= 30 | 3 | 10% 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 |
| # 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 |
|---|---|---|---|---|---|---|
| | RT DB-5 | RT DB -17 | MDL extrac t | PQL extract | MDL sample | PQL sample |
| | minute | minute | ug/L | ug/L | ug/L | ug/L |
| Alachlor | 25.6 | 17.4 | 80 | 320 | 0.16 | 0.64 |
| Ametryn | 25.6 | 18.8 | 5.0 | 20 | 0.010 | 0.040 |
| Atrazine | 20.0 | 14.7 | 5.0 | 20 | 0.010 | 0.040 |


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| Components | | | Water | Water | Water | Water |
|---|---|---|---|---|---|---|
| | RT DB-5 | RT DB -17 | MDL extract | PQL extract | MDL sample | PQL sample |
| Atrazine Desethyl | 10.22 | 12.22 | 5.0 | 20 | 0.010 | 0.040 |
| Atrazine Desisopropyl | 10.07 | 12.38 | 5.0 | 20 | 0.010 | 0.040 |
| Azinphos Methyl | 38.9 | 35.9 | 45 | 180 | 0.090 | 0.36 |
| Bromacil | 26.9 | 22.2 | 40 | 160 | 0.080 | 0.32 |
| Butylate | 12.5 | 8 | 25 | 100 | 0.050 | 0.20 |
| Chlorpyrifos Ethyl | 28.2 | 19.7 | 5.0 | 20 | 0.010 | 0.040 |
| Chlorpyrifos Methyl | 25.1 | 17.8 | 12 | 48 | 0.024 | 0.096 |
| Demeton | 12.2 | 12.4 | 12 | 48 | 0.0.024 | 0.096 |
| Diazinon | 21.7 | 14.7 | 15 | 60 | 0.030 | 0.12 |
| Disulfoton | 22.1 | 15.2 | 2.5 | 10 | 0.0050 | 0.020 |
| Ethion | 34.2 | 29.3 | 5.0 | 20 | 0.010 | 0.040 |
| Ethoprop | 16.8 | 12.2 | 2.5 | 10 | 0.0050 | 0.020 |
| Fenamiphos | 31.8 | 26.8 | 38 | 152 | 0.076 | 0.30 |
| Fonofos | 21.4 | 15.1 | 5.0 | 20 | 0.010 | 0.040 |
| Hexazinone | 35.8 | 33.4 | 35 | 140 | 0.070 | 0.28 |
| Malathion | 27.5 | 20.4 | 5.0 | 20 | 0.010 | 0.040 |
| Metalaxyl | 25.9 | 19.1 | 90 | 360 | 0.180 | 0.72 |
| Metolachlor | 28.0 | 19.1 | 60 | 240 | 0.12 | 0.48 |
| Metribuzin | 24.4 | 19.1 | 25 | 100 | 0.050 | 0.20 |
| Mevinphos | 12.4 | 9.9 | 15 | 60 | 0.030 | 0.12 |
| Naled | 9.5 | 6.7 | 40 | 160 | 0.080 | 0.32 |
| Norflurazon | 35.2 | 31.7 | 25 | 100 | 0.050 | 0.20 |
| Parathion Ethyl | 28.2 | 20.1 | 10 | 40 | 0.020 | 0.0.080 |
| Parathion Methyl | 25.0 | 18.4 | 5.0 | 20 | 0.010 | 0.040 |
| Pendimethalin | 17.6 | 19.6 | 111 | 444 | 0.22 | 0.88 |
| Phorate | 18.6 | 13.1 | 2.5 | 10 | 0.0050 | 0.020 |
| Prometon | 11.22 | 12.64 | 30 | 120 | 0.60 | 0.24 |
| Prometryn | 25.8 | 18.5 | 30 | 120 | 0.060 | 0.24 |
| Simazine | 19.7 | 14.9 | 5.0 | 20 | 0.010 | 0.040 |
| Terbufos | 21.1 | 14.0 | 2.5 | 10 | 0.0050 | 0.020 |

**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 | L-6 | L-5 | L-4 | L-3 | L-2 | L-1 | |
| NPD A MIX | | | | | | | | | |
| Ametryn | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Atrazine | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Atrazine Desethyl | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Chlorpyrifos | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |


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| Parameter | | Standard Solution (ug/L) | | | | | | | Spike Solution (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | ISTD | Intermediate | L-6 | L-5 | L-4 | L-3 | L-2 | L-1 | |
| Ethyl | | | | | | | | | |
| Parathion Methyl | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Disulfoton | NQ | 2500 | 250 | 100 | 500 | 25 | 17.5 | 10 | 400 |
| Ethion | TPP | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Ethoprop | NQ | 2500 | 250 | 100 | 50 | 25 | 17.5 | 10 | 400 |
| Hexazinone | TPP | 15000 | 1500 | 600 | 300 | 150 | 105 | 60 | 2400 |
| Malathion | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Metalaxyl | NQ | 20000 | 2000 | 800 | 400 | 200 | 140 | 80 | 3200 |
| Metribuzin | NQ | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| Mevinphos | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Norflurazon | TPP | 15000 | 1500 | 600 | 300 | 150 | 105 | 60 | 2400 |
| Phorate | NQ | 2500 | 250 | 100 | 50 | 25 | 17.5 | 10 | 400 |
| Simazine | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Terbufos | NQ | 2500 | 250 | 100 | 50 | 25 | 17.5 | 10 | 400 |
| | | | | | | | | | |
| **NPD B MIX** | | | | | | | | | |
| Alachlor | NQ | 30000 | 3000 | 1200 | 600 | 300 | 210 | 120 | 4800 |
| Azinphos Methyl | TPP | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| Atrazine Desisopropyl | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Bromacil | NQ | 20000 | 2000 | 800 | 400 | 200 | 140 | 80 | 3200 |
| Butylate | NQ | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| Demeton | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Diazinon | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Fonofos | NQ | 2500 | 250 | 100 | 50 | 25 | 17.5 | 10 | 400 |
| Fenamiphos | TPP | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| Methamidophos | NQ | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| Metolachlor | NQ | 30000 | 3000 | 1200 | 600 | 300 | 210 | 120 | 4800 |
| Monocrotophos | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Naled | NQ | 20000 | 2000 | 800 | 400 | 200 | 140 | 80 | 3200 |
| Parathion Ethyl | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Chlorpyrifos Methyl | NQ | 5000 | 500 | 200 | 100 | 50 | 35 | 20 | 800 |
| Pendimethalin | NQ | 20000 | 2000 | 800 | 400 | 200 | 140 | 80 | 3200 |
| Prometon | NQ | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| Prometryn | NQ | 10000 | 1000 | 400 | 200 | 100 | 70 | 40 | 1600 |
| | | | | | | | | | |

* 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


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**TABLE 5: QC MEASUREMENTS AND ACCEPTANCE CRITERIA**

| # | QC MEASUREMENT | ACCEPTANCE CRITERION | CORRECTIVE ACTION |
|---|---|---|---|
| 1 | LFB/Matrix spike recoveries | separate LFB/MS stats | Reanalyze/Re-extract/Flag/Comment |
| | LFB/MS precision | =/< 30 % | |
| 3 | Cal. Verification | +/- 10% | Re-run and recalibrate/Flag/Comment |
| 4 | Surrogate recovery NMX | 47-111% | Reanalyze/Re-extract/Flag/Comment |
| 5 | Internal standard recovery | 50%-200% | Reanalyze/Flag/Comment |
| 5 | QCS verification | +/- 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) | Maintain and re-run |
| 7 | Calibration Levels Calibration Fit Acceptance criterion | 3 levels linear 10%RSD, 5 level 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 expect value | Use appropriate cal fit/Re-run/ Recalibrate/Flag/Comment |

Statistical recovery limits for LFB/MS and surrogates recoveries are typically based on QC Manager statistics for the last one to two calendar years (if available). The limits are recalculated at least annually.The results of statistical calculations are saved at FLDEP1\DEAR\LABS\LAB5\CHEMISTRY\ORGANIC\QC LIMITS STATS. The statistical recovery limits are then entered into QC Manager limits tables. The initial QC limits are replaced with statistical ones whenever enough data points are accumulated. At least 20 points are required, but it is preferable to wait for about 50 points or more. If enough data points is available for LFBs but not for matrix spikes then LFB statistical limits may be applicable for both categories on temporary basis.
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 1mL GC 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.

All standard preparations are recorded in the Standard/Reagent Preparation Tracker. In order to prepare fresh standards go to LIMS-Technical-Standard/Reagent Preparation Tracker. Select GC from the pull down list. Hit "Reports" and then "History". When prompted enter the standard tracking number for the standard you are going to replace. Examine the "History Tree". An example of a "History Tree" is shown below:

History of Serial # 78000

78000-NPD A L1
77998-NPDA INT
77997-NPDA INT STOCK
77500-NPDA STOCK 02si
77996-NMX 1000 PPM
49067-NMX NEAT
77669-ISTD INT
77668-ISTD STOCK
68690-TPP NEAT
58274-5-NITROQUINOLINE.

In order to get exact information on how the standard was prepared look at "history data sheets" that will show exact information on standards preparations. Before preparing new standards consult with the GC group supervisor whether any changes to standards preparation procedures should be made. Those may include different prepared volumes, concentrations, new, additional concentration levels, etc.

All freshly prepared standards need to be entered in the Standard Preparation Tracker.

# 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.


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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.
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.


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## 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.<br>The statistical limits formula for surrogate recoveries have been updated.<br>Updated standard preparations.<br>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. |
| 01/05/2017 | Added prohibition for “include origin” option for calibration fits. Removed tests W-PESTNP-R for water samples due to replacement of that analysis with GC/MS/MS. Test W-PESTNP-R will be removed from LIMS. Updated standard and spike concentrations in Table 4. Added chapter 9.1.3 “instrument maintenace after runs with poor data quality” Updated standards preparation chapter. |
| 01/03/2018 | Updated QC limits, Edited tables. Number of mixes reduced to two. |
| 01/02/2019 | Updated QC limits, MDLs/PQls and standard mixes. Removerd soil/waste tests. Added Masshunter software. |
| 12/18/2019 | Removed the SPLP test and references to method 8141B. Updated initial calibration chapter and annual MDL verifications chapter. Updated MDLs |


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