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Agricultural Marketing Service, Science & Technology
Pesticide Data Program

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Revision: 7	Replaces: 04/01/18		Effective: 03/01/20

1. Purpose:

To provide standard procedures for:
- instruments, equipment and injection sequence used in the USDA/AMS Pesticide Data Program (PDP). See SOP PDP-ADMIN for administrative requirements, (e.g., purchase approval, PDP Equipment Inventory System, Instructions for Permission to Salvage, Transfer or Dispose of Equipment, etc.).
- quantitative and qualitative analysis of pesticide residues determined for the USDA/AMS PDP.
- data reduction, reporting, and submission by participating laboratories.

2. Scope:

This standard operating procedure (SOP) shall be followed by all laboratories conducting residue studies for PDP, including support laboratories conducting stability or other types of studies that may impact the program.

3. Outline of Procedures:

5. Instrumentation
5.1 SOPs and Manuals
5.2 Maintenance
5.3 Performance Verification
5.4 Records

6. Calibration
6.1 Calibration Integrity
6.2 Quantification Using Calibration Curves
6.3 Quantification Using Single Point Comparisons
6.4 Quantification of Multi-Peak Compounds
6.5 Quantification of Spikes

7. Generating Raw Data
7.1 Injection sequence description
7.2 Retention Time Criteria (Selective Detection and MS Systems)

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4.　　References:

- US EPA, *Maintenance and calibration of equipment,* 40 CFR 160.63.
- US EPA, *Standard operating procedures,* 40 CFR 160.81.

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- US EPA, *Conduct of a study,* 40 CFR Part 160.130
- US EPA, *Appendix A*, 40 CFR Part 136
- US EPA, *Reporting of study results,* 40 CFR Part 160.185
- US EPA, *Tolerances and Exemptions from Tolerances for Pesticide Chemicals in Food,* 40 CFR Subchapter E, Part 180
- US EPA/OPPTS, *Processed Food/Feed*, 860.1520
- FIFRA, *Pesticide Emergency Exemptions*, Section 18, 40 CFR Part 160
- FDACS, *QA/QC Guideline Document,* Section 14
- USDA/FDA, *Food and Drugs,* 21 CFR Part 175.105
- FDA Center for Veterinary Medicine, *Guidance for Industry: Mass Spectrometry for Confirmation of the Identity of Animal Drug Residues, Final Guidance,* US Department of Health and Human Services, Rockville, MD, Guide #118, May 1, 2003. http://www/fda/gov/cvm/guidance/guide118.pdf
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- Sphon, J.A. *Use of Mass Spectrometry for Confirmation of Animal Drug Residues*, J. Assoc. Off. Anal. Chem. 61 (1978) 1247-1252

5.   Instrumentation

5.1   SOPs and Manuals

Each laboratory shall develop SOPs for PDP equipment operation. The SOPs shall set forth in sufficient detail the methods, materials, and schedules to be used in the routine inspection, cleaning, maintenance, testing, calibration, and/or performance verification of equipment used, and shall, when appropriate, specify remedial action to be taken in the event of failure or malfunction of equipment. SOPs and operator manuals shall be readily accessible to applicable laboratory staff. Manufacturer's manuals or published literature may be used as a supplement to SOPs.

5.2   Maintenance

All instruments and other equipment used in the analysis of PDP samples shall be inspected, cleaned, and maintained in proper working condition so that the accuracy, precision, and sensitivity requirements specified in this SOP and SOP PDP-QC are met.

5.3   Performance Verification

Before being placed into service, an instrument shall undergo appropriate checks to establish that all requirements are met. See SOP PDP-QC.

5.4   Records

5.4.1 Records (e.g., logbooks) shall be maintained for all critical equipment and instruments. These records shall be used to document all routine and non-routine inspection, maintenance, and calibration activities, including the date, the identity of the personnel performing the activities, and any maintenance (routine or otherwise), repairs, or remedial actions.

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5.4.2   Data packages shall reflect the specific instruments and equipment that were used to generate, measure, or assess the data. Data on the performance verification of instruments (e.g., gas chromatograph-mass selective detector (GC-MSD), etc.) utilized in the analysis of a data set are to be maintained by the laboratory. See Section 8 of this SOP for hardcopy data package requirements. See Section 7 of this SOP for mass spectrometry (MS) documentation requirements.

5.4.3   Calibration and/or performance verification data for balances, refrigerators, and other peripheral equipment do not need to be included in the hardcopy data packages, but shall be maintained by the laboratory.

5.4.4   See SOP PDP-ADMIN for records storage and archival requirements.

6.   Calibration

Instruments and equipment that have significant effects on test results shall be calibrated at the minimum frequency specified in the laboratory's internal SOPs.

6.1   Calibration Integrity

6.1.1   Calibration integrity is defined as steady instrument response to a given amount of analyte over the duration of a sample run. Calibration integrity shall be determined by injecting standards at the beginning and end of a run to evaluate the variability in instrument response and any changes in retention time (see 6.1.2). Injection of a standard(s) between the beginning and end of a run also may be required. Calibration integrity shall be calculated in terms of relative percent difference (RPD), percent difference (%D), or percent relative standard deviation (%RSD) using the following equations:

$$RPD = \frac{|X_1 - X_2|}{\left[\frac{X_1 + X_2}{2}\right]} \times 100$$

where X_1 is the response of the first analytical standard injected and X_2 is the response of the second standard injected;

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$$\%D = \frac{C_1 - C_2}{C_1} \times 100$$

where C_1 is the known concentration of the standard used for quantification and C_2 is the concentration of that standard calculated using the calibration curve;

$$\%RSD = \frac{SD}{avg.\ RF} \times 100$$

where SD is standard deviation:

$$SD = \sqrt{\frac{\sum\limits_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

and RF is response factor, or the area or height of each standard divided by the concentration of that standard.

6.1.2 Standard response drift greater than 20% RPD, %D, or RSD indicate that additional standards within the run may be injected in order to attempt to meet the required 20% calibration integrity requirement. Each laboratory shall document exceptions in internal SOPs and shall determine the number of intermediate standards required throughout the run to maintain calibration integrity.

6.1.3 For cases where no residues were detected in samples and only the spike recovery is being quantitated, the requirement for calibration integrity shall be 30%.

6.2 Quantification Using Calibration Curves

6.2.1 Incurred residue levels may be subtracted from matrix matched standards prior to generating the calibration curve. A laboratory may elect to subtract incurred residue levels if the following conditions are met:

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- Blank matrix cannot be obtained. The laboratory shall make every effort to obtain blank matrix such as purchasing organic produce, saving analyzed samples that are pesticide free, etc.

- The incurred residue level is less than 2xLOQ.

If a laboratory elects to subtract incurred residues from matrix matched standards, they shall have internal procedures on how to handle the subtraction process.

6.2.2 If calibration curves are used for quantification, they shall be constructed using standards which bracket the expected range of residue concentration. A suggested range is 1xLOQ to 10xLOQ. Second-order curves (i.e., quadratic) may be employed, providing that a sufficient number of points (i.e., minimum of five) is used to define the curve.

6.2.3 For any analyte that is quantitated using a calibration curve, the fitness of curve, whether first- or second-order, **shall** be demonstrated in the same injection sequence used to report the data by one of the following accepted methods:

- correlation coefficient (where $R \geq 0.995 / R^2 \geq 0.990$),
- percent relative standard deviation (where %RSD $\leq$ 20), or
- percent difference of calculated vs. known standard concentration in the curve (where %D is within 20%).

6.2.4 The laboratory shall specify in an internal SOP the method/parameter(s) used to demonstrate fitness of curve.

6.2.5 Results obtained using a calibration curve shall lay within the range of the calibration curve. If results fall outside the calibration curve, the sample must be diluted, the calibration curve extended, or the procedures for single point comparisons followed. The procedure for extending the range of the calibration curve shall be documented in internal laboratory procedures. Data generated to support extension of the calibration curve shall be maintained and housed with the QAU.

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If method range has been extended beyond the highest validated level, then samples may be diluted for quantitation purposes; however, dilutions must be done proportionally with matrix so that the matrix concentration of the sample is similar to that of the analytical standards used to prepare the calibration curve.

6.3   Quantification Using Single Point Comparisons

Quantification using a single standard is permitted if the sample response is within 30% of the standard response for samples greater than LOQ; if it is not, dilution of the sample or injection of a different standard concentration shall be required. This difference shall be calculated using the following equation:

$$\frac{X_{standard} - X_{sample}}{X_{standard}} \times 100$$

where $X_{standard}$ is the response of the standard and X_{sample} is the response of the sample.

6.4   Quantification of Multi-Peak Compounds

Quantification of multi-peak compounds may be based on the largest peak or the sum of all of the peaks. When reporting multi-peak compounds as total (combined) values and one or more peaks are Below Quantifiable Level (BQL), determine and report the value(s) for the BQL peak(s) using either single point quantification or the value calculated by the data station based on the calibration table. If one or more peaks are less than the Limit of Detection (LOD), or LOQ where LOD=LOQ, do not include them in calculating the total (combined) value. In either case, code the reported value as an estimate "E" in the quantification field of the analytical results section.

6.5   Quantification of Spikes

6.5.1   Incurred residue levels may be subtracted from spike recovered prior to calculating the percent recovery. A laboratory may elect to subtract incurred residue levels if the following conditions are met:

- Blank matrix cannot be obtained. The laboratory shall make every effort to obtain blank matrix such as purchasing organic produce, saving analyzed samples that are pesticide free, etc.

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- The incurred residue level is less than 2xLOQ.

- The laboratory shall report blank subtracted spike recovery data by entering the amount subtracted into the comments field and entering an "S" (Incurred Subtracted) code in the Exception field for that compound on the QA/QC Recovery section of the RDE.

If a laboratory elects to subtract incurred residues, they shall have internal procedures on how to handle the subtraction process.

6.5.2 When a 2xLOQ spike recovery value falls below 50%, by definition, these spikes are quantitated using responses less than the LOQ. This is an acceptable PDP practice.

6.5.3 Incurred residues, as determined using the matrix blank, shall not be subtracted from the spike when the residue in the matrix blank exceeds 2xLOQ. If an incurred residue is greater than 2xLOQ or otherwise prevents reporting of an associated QA/QC recovery, an "I" (Incurred Residue) code shall be entered into the Exception field for that compound on the QA/QC Recovery section of the RDE for recoveries that are reported.

6.5.4   Pesticides not recovered shall be reported using an "N" (Not Recovered) code in the Exception field for that compound on the QA/QC Recovery section of the RDE for the spiked pesticide.

6.5.5 Pesticides reported as estimates shall be coded as "E" (Estimate) in the Exception field for that compound on the QA/QC Recovery section of the RDE for recoveries that are reported.

6.5.6 Pesticides reported as having matrix interference shall be coded as "M" in the Exception field for that compound on the QA/QC Recovery section of the RDE.

6.5.7 Pesticides reported as Marginal Performing Analytes shall be coded as "P" in the Exception field for that compound on the QA/QC Recovery section of the RDE.

6.5.8 Pesticides reported as unvalidated shall be coded as "U" in the Exception field for that compound on the QA/QC Recovery section of the RDE (refer to *Attachment 2,*

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Flowchart for reporting codes).

7. Generating Raw Data

7.1 Injection sequence description

7.1.1 Each laboratory shall develop an SOP detailing an appropriate injection sequence in order to ensure data integrity and uniform response across the sample set. "Uniform response" shall be construed as no greater than 20% RPD, %D, or RSD between calibration responses (refer to Section 6.1 of this) or 30% if a residue was not detected and only the spike is being quantitated.

7.1.2 Standards for each compound analyzed shall be included with every injection sequence. It is recommended that standards spanning the expected range of residue concentrations, such as 1xLOQ to 10xLOQ, be included in the sequence to allow construction of a calibration curve; however, construction of a calibration curve is not required unless a curve is used for quantification.

7.1.3 Standards must be run at a minimum of the beginning and end of the data run to demonstrate calibration integrity. This may be accomplished via a single standard or a full set of calibration curve standards.

7.1.4 Each initial analytical run shall include the reagent blank, matrix blank, spikes, and samples. For additional runs (i.e., reinjects/dilutions) QC samples shall be run as necessary (i.e. reagent or matrix interference).

7.1.5 A non-extracted LOD standard for each compound analyzed shall be run with each data set as a diagnostic tool (i.e., the laboratory is not required to calculate signal-to-noise ratio (s/n), but the peak must be observable). If the peak is not observable, the laboratory shall take the appropriate action (e.g., raise the LOD, re-inject the standard, etc.). For laboratories that use in-matrix calibration standards, the LOD standard shall also be in-matrix. For laboratories that do not use in-matrix calibration standards, the LOD standard shall be in the same solution as the calibration standards.

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7.2 **Retention Time Criteria (Selective Detection and MS Systems)**

7.2.1 GC Retention Time

7.2.1.1 If an external standard is used, the retention time (RT) of the compound of interest in the standard and the RT of the same compound in the sample shall be within 0.1^{1} minutes.

7.2.1.2 If an internal standard is used, the relative retention time (RRT) of the compound of interest to the internal standard within the reference standard and the RRT of the compound of interest to the internal standard within the sample shall be within 0.01 minutes.

7.2.2 LC Retention Time

7.2.2.1 If an external standard is used, the RT of the compound of interest in the standard and the RT of the same compound in the sample shall be within 0.1^{1} minutes.

7.2.2.2 If an internal standard is used, the RRT of the compound of interest to the internal standard within the reference standard and the RRT of the compound of interest to the internal standard within the sample shall be within 0.1 minutes.

7.2.3 MS Screening for Identification

In order to maximize the number of compounds screened by MS systems while maximizing the number of scans per second and dwell times, it may be desirable to perform the initial identification and quantification using fewer than three ions for some or all of the compounds. Presumptive-positive samples shall be re-injected or data reprocessed to meet all MS confirmation criteria.

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[1] The laboratory may perform instrument-specific retention time studies to verify stipulation of different retention time window criteria than those specified in this SOP. It is expected that a generally accepted method of retention time window calculation be used and documented to establish these criteria.

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7.3 Confirmation Procedures for Selective Detection Systems

7.3.1 Where possible, mass spectral confirmation is preferred. All residues detected at concentrations that are equal to or greater than the established and verified LOD for a given analyte shall be confirmed. The method available for confirmation shall be capable of detecting the desired residue at a concentration that is equal to or less than the concentration quantitated by the primary instrument. All residues that cannot be confirmed shall be reported as non-detects. The confirmation method shall be reported (refer to *Attachment 1, PDP Laboratory Information Form (LIF) Codes*).

7.3.2 When more than one confirmation method has been utilized, the method with the higher level of confidence shall be entered in the Confirmation Method 1 field and the method with the next highest level of confidence should be entered in the Confirmation Method 2 field. For example, if a residue is confirmed using an alternate column and mass selective detector: the laboratory would most likely enter "M" in the Confirmation Method 1 field and "C" in the Confirmation Method 2 field of the RDE. The decision regarding the level of confidence of a particular confirmation is left to the discretion of the Technical Program Manager.

Note: The Ident Points (identification points) field of the RDE is an optional field that may be used to record the degree of confirmation.

7.3.3 Acceptable confirmation methods for GC and LC analyses (element specific/selective detectors) are:

- Alternate detector (element specific/selective detectors, including various forms of mass spectrometry). All applicable confirmation criteria for that detector must be met.
- Alternate column, provided the alternate column changes the elution order or significantly changes (i.e., 2 or 3 peak widths) the retention time (RT) of the detected pesticides.
- Alternate mobile phase, provided the alternate mobile phase changes the elution order or significantly changes (i.e., 2 or 3 peak widths) the RT of the detected pesticides is an acceptable confirmation method only for LC analysis (element specific/selective detectors).

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7.4 MS Confirmation Criteria

7.4.1 GC/MS and LC/MS Confirmation Criteria

7.4.1.1 A minimum of three structurally significant ions (meeting the 3:1 s/n ratio) are required for confirmation. For GC/MS, because the molecular ion is the most structurally significant ion in a mass spectrum, if it is present and meets the 3:1 s/n ratio, it is preferable that it be included as one of the three ions.

Note: If instrument conditions and/or ionization techniques limit the number of ions available, the laboratory shall request a deviation from MPD in order to report results under these conditions.

7.4.1.2 A pair of isotopic cluster ions may be used as two of the three structurally significant ions required for confirmation.

7.4.1.3 Use of fragment ions resulting from water loss to meet the three structurally significant ions requirement is discouraged.

7.4.1.4 The confidence limits of the relative abundance of structurally significant ions used for SIM and/or full scan identification shall be ± 30% (relative) when compared to the same relative abundances observed from a standard solution injection made during the same analytical run.

7.4.1.5 MS spectra produced by "soft" ionization techniques (e.g., GC/MS - chemical ionization and for LC/MS – APCI, APPI, ESI, etc.) may require additional evidence for confirmation. If the isotope ratio of the ion(s) or the chromatographic profile of isomers of the analyte is highly characteristic, there may be sufficient information for confirmation. Additional evidence may consist of MS/MS data, use of a different ionization technique, use of a different chromatographic separation system, and for LC/MS systems, altering fragmentation by changing ionization conditions.

7.4.1.6 GC/MS: Fragmentation that results from "soft" ionization techniques is highly dependent on instrument design and the conditions applied (i.e., the obtained spectra can widely differ). Commercially available spectral libraries bundled with

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GC/MS instruments may contain spectra generated under standard 70eV EI conditions; therefore, the use of library search software for spectra from "soft" ionization techniques could result in identification errors and is discouraged.

7.4.2 GC/MS/MS and LC/MS/MS Confirmation Criteria

7.4.2.1 Target analyte confirmation shall be performed by either (1) monitoring the transition of one precursor ion to at least two product ions, OR (2) monitoring at least two precursor-to-product ion transitions.
Multipeak compound confirmation may be based on the largest peak or the sum of all the peaks. If it is based on the sum of all the peaks, one or two of the constituents can be used for both transitions.

Note: If instrument conditions and/or ionization techniques limit the number of transitions available, the laboratory shall request a deviation from USDA/AMS in order to report results under these conditions.

7.4.2.2 The abundance of the signal from the precursor-to-product ion transition shall meet the 3:1 s/n ratio requirement.

7.4.2.3 The relative abundances of ion transitions used for compound identification in the sample shall be ± 30% (relative) when compared to the same relative abundances observed from a standard solution analyzed during the same analytical run if more than one precursor-to-product ion transition is monitored. The ion ratio tolerance shall be calculated using the following example: If the ion ratio (qualifier area count/target area count) is 15%, the acceptable range will be 15%+/-4.5 or 10.5% to19.5%.

7.4.2.4 Use of product ions resulting from water loss for identification is discouraged.

Note: Any information that provides a contraindication of identity of the residue will be addressed in the internal SOP by the laboratory.

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7.5   MS Documentation Criteria

Structurally significant ions and/or precursor-to-product ion transitions used for confirmation shall be documented.

8.   Data Handling

8.1   Raw Data Handling

8.1.1. Hardcopy raw data are defined as any laboratory worksheets, logbooks, records, notes, chromatograms, calculations, instrument printouts, and any other data, which are the result of original observations and activities. Electronic raw data are the files generated by the instrument system.

8.1.2 For manual entry, hardcopy raw data shall be recorded directly, promptly, and legibly in permanent ink. Pencil or erasable pen is not acceptable. All data entries shall be dated on the date of entry and signed or initialed by the person entering the data. Each individual error shall be corrected using a single-line cross out (no white-out). It is recommended, but not required, that the reason for the correction be indicated. Each correction shall be dated and initialed. Documented error codes may be used to explain errors. Correction of multiple errors may be accomplished in the following manner:

- On first occurrence of the error, or on a summary sheet, make/indicate the appropriate correction, including date, initials, explanation of error/error code, and all affected subsequent entries.
- Each subsequent occurrence of the error must then be corrected, dated, and initialed.

8.1.3 Each participating laboratory shall ensure sample and data traceability for raw and electronic data collection and processing. Chromatograms that have been reprocessed through the data system shall be clearly labeled.

8.1.4 Each participating laboratory shall maintain a log of names, initials, and signatures for all individuals who are responsible for signing or initialing any laboratory record.

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8.2 Hardcopy Data Package Requirements

8.2.1 Routine sample data packages and method validation data packages retained by the participant laboratory shall consist of laboratory records (i.e., worksheets and/or completed forms), USDA collection and report forms (where applicable), and supporting technical data in the form of chromatograms and integration reports, calculations, and derived data. Data requirements consist of two types, instrument and chromatographic. The following information shall be included in the data package.

8.2.1.1 The instrument method shall be included or referenced. Instrument information shall be traceable. Examples may consist of instrument type and identifier, detector type, injection volume, temperature parameters (injector, detector, oven), analytical column parameters (phase, film thickness, diameter, length), and instrument parameters (integration threshold, attenuation, timed events).

8.2.1.2 Chromatographic information shall be traceable. Examples may consist of sample ID, analyst name, dilution information, and date and time of injection.

8.2.2 At a minimum, hardcopies of data sets shall include the following:

- Instrument methods, or references to them (data acquisition, calibration/standardization, and data analysis parameters)
- Injection sequences
- Chromatograms and/or instrument reports of samples, standards, reagent blanks, matrix blanks, and matrix spikes
- PDP Sample Information Forms (SIFs) [if paper SIFs were submitted by the Sample Collector]
- Matrix blank, reagent blank, matrix spike, and sample results
- Documentation of technical and QA review

Note: Laboratories that choose to retain electronic data sets as.pdf or Excel files shall ensure all requirements for QA, traceability, etc. are met. Nothing shall be lost in the electronic domain that would normally be captured on paper, and all markups of the original chromatogram shall also be retained.

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8.2.3 Hardcopies of method validation data packages submitted to USDA/AMS shall include copies of the summary reporting forms, narrative describing the method, and cover memo submitted to the PDP Technical Director, Method Validation Coordinator, and liaison chemist (refer to SOP PDP-QC).

9. Data Reporting

9.1 Calculations and Significant Figures

9.1.1 Each laboratory shall have an internal SOP describing the data processing steps taken to reach the final reported concentration. Data shall not be ignored without a written explanation (e.g., instrument malfunction, wrong standard used, co-eluting peak, etc.).

9.1.2 In calculations, at least one significant figure in excess of the reporting requirements shall be carried through the calculation. When rounding is required, values greater than or equal to 5 shall be rounded up.

9.1.3 Percent recoveries shall be reported to two significant figures if less than 100 or to three significant figures if greater than 100.

9.1.4 Concentrations shall be reported to at least two significant figures in parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt). The laboratory may elect to report more than two significant figures. If more than two significant figures are reported, it is the laboratory's responsibility to determine the appropriate number of significant figures for each commodity/pesticide pair using a given method.

9.1.5 Individual peaks may be reported for multiple peak compounds. If separate standards are available for separate isomers, it is preferable to report the isomers separately.

9.2 Determination of Residue Concentrations for PDP Reporting Purposes

9.2.1 A laboratory may elect to set LOD = LOQ provided all of the following conditions are met:

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- the analyses are completely performed via MS systems (i.e., quantification and self-confirmation) **and**
- the qualifier ions are at least 3 x s/n **and**
- the quantification ions have a response at least 10 x s/n.

The laboratory shall code the findings (both detects and non-detects) as "Z" [LOD equals LOQ] in the "Test Class" section of the RDE analytical results section only if the actual LOQ value is not entered for the findings.

9.2.2   Do not report residue concentrations less than the verified LOD.

9.2.3   Compounds appearing on the analytical results list for which results are not/cannot be reported shall be coded as "M" [not analyzed (e.g., compound not in standard, used as marker only)] or "UD" [unable to determine (e.g., matrix interference, method failure)] in the mean result field of the RDE analytical results section.

9.2.4   Numeric concentrations below the LOQ are considered low confidence values associated with a qualitative finding. A concentration value is not required when a pesticide is detected at or above the determined LOD and below the determined LOQ. The laboratory shall code the finding as "Q" (residue BQL) in the "Annotated Info." section of the RDE analytical results section. The concentration will be converted to ½ LOQ in the PDP database for reporting purposes.

9.2.5   All detections shall be coded as:

- "O" (detect – original extraction value);
- "A" (detect – average of original and re-extraction analyses values); or
- "R" (detect – re-extraction analysis value)

in the mean result field of the RDE analytical results section (refer to *Attachment 2, Flowchart for Reporting Codes)*.

9.2.6   Validated Pesticide/Commodity Pairs

A pesticide/commodity pair is considered validated when all applicable modules in SOP

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PDP-QC have been met.

9.2.6.1 Results less than the verified LOD shall be coded as "ND" (non-detect, well-recovered analyte) in the mean result field of the RDE analytical results section.

9.2.6.2 Residue concentrations greater than or equal to the LOQ shall be reported on the RDE analytical results section. If there are no qualifications of the data (i.e., estimate, marginal performing analyte, unvalidated compound), the quantification field shall be left blank. If the data is an estimate (e.g., has failed linearity, calibration integrity or spike recovery), then the results shall be coded as "E" (estimate) in the quantification field of the RDE analytical results section (refer to *Attachment 2, Flowchart for Reporting Codes)*.

9.2.7 Validated Marginal Performing Analytes

Marginal Performing Analytes are identified and documented during method validation or during ongoing QC.

9.2.7.1 Results less than the verified LOD shall be coded as "NP" (non-detect, marginal performing analyte) in the mean result field of the RDE analytical results section.

9.2.7.2 Residue concentrations greater than or equal to the LOQ shall be reported on the RDE analytical results section. Results shall be coded as "P" (marginal performing analyte) in the quantification field of the RDE analytical results section (refer to *Attachment 2, Flowchart for Reporting Codes)*.

9.2.8 Unvalidated Pesticide/Commodity Pairs

As a rule, unvalidated residues should not be reported. However, unvalidated residues may be reported on a case-by-case basis. For example, identification and tentative quantification of a compound not currently included in the analytical screen or preliminary results for special projects. Procedures to be followed in these instances are as follows:

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9.2.8.1 Results less than the estimated LOD shall be coded as "NU" in the mean result field of the RDE analytical results section.

9.2.8.2 Residue concentrations greater than or equal to the LOQ shall be reported on the RDE analytical results section. Results shall be coded as "U" (unvalidated analyte) in the quantification field of the RDE analytical results section (refer to *Attachment 2, Flowchart for Reporting Codes)*.

9.2.9 In cases where calibration integrity exceeds 20%, the laboratory shall use best professional judgment to determine whether or not to report positive findings as follows:

- Report positive findings using quantification codes: "E" (Estimate), "P" Marginal Performing Analyte, or "U" (Unvalidated Compound). The use of code "E" does not require a deviation letter and should be determined on a set-to-set basis, using best professional judgment. It could be used when the calibration integrity, linearity, or the spike recovery fail.

- Report results that could not be quantified as non-detects using mean result code "UD" (refer to *Attachment 2, Flowchart for Reporting Codes)*.

9.3   Administrative Reporting Level

The Administrative Reporting Level is a level below which results shall be reported as not detected. For all commodities, it is 1 ppb (parts per billion). A laboratory's reported LOD may be at or above this level, but not below.

9.4   Reporting o-Phenylphenol

O-phenylphenol has multiple uses as an antimicrobial agent. It is listed in 21 CFR as an indirect food additive as a component of a sanitizing solution. O-phenylphenol also has a number of tolerances established for various food commodities. Therefore, when detected, it cannot be determined whether residues result from the application of o-phenylphenol to a given commodity or from unintended contact with o-phenylphenol via packaging or environmental sources such as typical cleaning agents. PDP's reporting policy for residues of o-phenylphenol for all commodities is as follows:

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- If no tolerance is established for a given commodity, o-phenylphenol will not appear on that commodity's list of requested compounds. Do not validate or report o-phenylphenol for that commodity.
- If a tolerance is established, o-phenylphenol will appear on that commodity's list of requested compounds. Attempts shall be made to validate and report o-phenylphenol.

9.5   PDP Tolerance Table

9.5.1   USDA/AMS maintains a PDP Tolerance Table adapted for current PDP samples. The table is available to PDP participants on the USDA/AMS Extranet. It lists tolerances (and FDA action levels for compounds with revoked tolerances that are persistent and may still be found) for many but not all registered pesticides on current PDP commodities and may or may not include the same compounds as those listed in a particular Commodity Compound List Memorandum (also available on the USDA/AMS Extranet). The PDP Tolerance Table includes permanent, interim, regional, and Section 18 emergency tolerances. Blank spaces in the table indicate that no tolerance is established. Tolerances for metabolites are based on the parent unless there is a specific tolerance for the metabolite.

9.5.2   The PDP Tolerance Table is intended to be used only as a general guide and is prepared for the convenience of the participants. The tolerance information should not be used for enforcement, or domestic/international trade issues, without verifying the completeness and accuracy of this tolerance information. The information may be out-of-date because new pesticide tolerances may be promulgated by EPA at any time and existing tolerances may be revised/revoked at any time following EPA review. EPA's new/revised/revoked tolerances are published as issued in the daily Federal Register. The US Tolerance Tracker (formerly the Pesticide Chemical News Guide) is a monthly subscription service that reviews tolerance information published in the Federal Register and publishes cumulative monthly updates. The PDP Tolerance Table is updated approximately quarterly to reflect any changes to pesticide-commodity tolerances. Laboratories are encouraged to notify USDA/AMS if they become aware of any newly registered pesticides or find errors in the PDP Tolerance Table.

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9.6   Non-violative results

Non-violative results for PDP reporting purposes are residue determinations that do not exceed a stated tolerance. A tolerance is the maximum amount of a pesticide residue that is permitted in or on a food. All concentrations shall be reported on the RDE analytical results section.

- A detected residue concentration is considered to be non-violative if it is equal to or less than the 40 CFR 180 tolerance for the given commodity.
- If no commodity tolerance exists then the group tolerance (if available) should be used.
- If no commodity or group tolerance is established or Section 18 reference noted, the tolerance shall be considered zero.

9.7   Presumptive Tolerance Violations (PTV)

Tolerances are established for food commodities by EPA under the authority of the Federal Food, Drug, and Cosmetic Act (FFDCA) and are listed in 40 CFR 180. Tolerances are usually established for a specific commodity, however, tolerances may also be established by the commodity groupings established by EPA in 40 CFR 180 or Section 18 tolerances may apply.

9.7.1   A residue is considered to exceed the 40 CFR 180 tolerance when the reported value exceeds the tolerance by one number in the second significant figure, or in the case of a single significant figure in the tolerance expression, by one number in that significant figure. For example, if the tolerance is 20 ppm, then a "presumptive violation" would occur at 21 ppm. If the tolerance is 1.0 ppm, then a "presumptive violation" would occur at 1.1 ppm. If the tolerance is 1 ppm, then a "presumptive violation" would occur at 2 ppm.

9.7.2   If the pesticide residue exceeds the established tolerance or does not have an established tolerance, the laboratory shall report the appropriate code in the annotated information field of the RDE analytical results section (refer to *Attachment 1 – Laboratory Information Form (LIF) Codes*).

9.7.3   PTV Notification Policy

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PTVs shall be transmitted via RDE during normal data submission process. USDA/AMS shall notify HQ FDA. If States have a cooperative agreement with local FDA, USDA/AMS will also send a State-specific report to the laboratories, if requested.

9.8   Tolerance Interpretation for Processed Commodities

9.8.1   USDA/AMS shall follow the guideline of the EPA Office of Prevention, Pesticides and Toxic Substances (OPPTS) 860.1520, processed food/feed, section (b), which states in part:

"If residues do concentrate in a processed commodity, a food or feed additive tolerance must be established under section 409 of the Federal Food, Drug and Cosmetic Act (FFDCA) (or a section 701 Maximum Residue Limit (MRL) in some cases). However, if residues do not concentrate in processed commodities, the tolerance for the raw agricultural commodity (RAC) itself applies to all processed food or feed derived from it."

9.8.2   When a specific tolerance for a compound is listed for a processed commodity in the Code of Federal Regulations (CFR), that tolerance will be stated in the quarterly tolerance tables. For example, 40 CFR 180.472 lists a specific tolerance for imidacloprid in tomato paste at 6.0 parts per million (ppm). This is the tolerance that will be listed for tomato paste in the tolerance table scheduled for next quarterly release.

9.8.3   If a specific tolerance for a compound is not listed in the CFR for a processed commodity, then the tolerance for the RAC will be listed in the PDP tolerance table. For example, 40 CFR 180.303 does not list a specific tolerance for oxamyl in tomato paste; however, there is a tolerance of 2 ppm for oxamyl on tomatoes, the RAC. A tolerance of 2 ppm for oxamyl will be listed for tomato paste in the next released tolerance table.

9.8.4   For juices, the tolerances for the RAC will be listed in the tolerance tables unless specific tolerances for juices are listed in the CFR. When adding water to juice concentrate, do not back-calculate for the water added. Reconstituted juices should be treated the same as ready-to-serve (RTS) juices. USDA/AMS will apply the RAC tolerance for a compound, as is, to RTS juice unless there is a specific juice tolerance in the CFR. For example, 40 CFR 180.608 lists a tolerance for spirodiclofen in grape juice at 2.4 ppm. This tolerance applies to both the RTS juice and the grape juice concentrate, after it is

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reconstituted. A tolerance of 2.4 ppm for spirodiclofen in grape juice is reflected in the current tolerance table. Another example is that 40 CFR 180.157 does not list a specific tolerance for mevinphos in grape juice. However, there is a specific tolerance listed at 0.5 ppm for grapes, the RAC. A tolerance of 0.5 ppm for mevinphos for the RAC is reflected for RTS grape juice and grape juice concentrate, after it is reconstituted, in the current tolerance table.

9.9   Reporting Proficiency Testing (PT) Results

Results for PT rounds issued by the CDFA-QAU and FAPAS shall be reported according to the provider's instructions. Laboratories also may report PDP PT results to USDA/AMS via RDE.

10.   Data Review

10.1   Each data package shall undergo review by the technical and QA sections for accuracy and completeness, adherence to PDP criteria, and integrity of the overall quality system. The QAU shall have access to all documentation necessary to achieve this objective. Both technical and QA reviews shall be documented.

10.2   Following QAU review of a data package, that data shall not be changed by any laboratory personnel unless as a response to comments/concerns/recommendations by the QAU. Actions taken as a result of technical and/or QA findings shall be documented.

11.   Remote Data Entry (RDE) System

11.1   RDE System Administration

11.1.1 Each laboratory and/or TPM shall designate an individual or individuals to administer applicable aspects of the RDE system. An existing laboratory system administrator can grant system administrator privileges to other users or USDA/AMS can provide a temporary account/password that connects directly to the RDE System Admin menu so that system administrator privileges can be granted to any user.

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11.1.2 The laboratory system administrator shall contact USDA/AMS to request new RDE user accounts for laboratory personnel. USDA/AMS shall create the user account in the central RDE database, then generate and send the laboratory a text data file holding the new account information. The laboratory system administrator shall then import the text data file to add the user using the Import New User feature on the RDE Manage User Accounts screen. Each user account shall be assigned one or more roles, which serve as defined permissions to access the different RDE options, based on position requirements.

11.1.3 The laboratory system administrator may reset passwords and unlock accounts as needed using the Manage User Accounts option in the RDE System and shall disable the RDE user account when an individual terminates employment with the organization.

Note: The RDE system will automatically deactivate any account not accessed in the past 90 days.

11.1.4 The laboratory system administrator shall import updates to standardized code look-up tables, like the commodity and site tables, using text data files provided by USDA/AMS and the Import Look-up Table Updates option on the RDE System Admin menu. USDA/AMS shall provide those updates quarterly in response to scheduled program changes or immediately if a new required code is added.

11.2 RDE System Access

11.2.1 The distributed RDE system requires Microsoft Office 2013 (V15.0) or newer, either 32-bit or 64-bit, installed on each client computer to run the application, including Access, Excel (for data exports), and Outlook (for data transmits). For optimal performance, the front-end application files should be installed on each client computer with connections to the single set of shared back-end database files.

11.2.2 The RDE system requires an assigned user account and password to gain access. Laboratory personnel shall contact the assigned laboratory system administrator to resolve problems with accessing the RDE system, such as a locked account or forgotten password. If the laboratory system administrator is not available, USDA/AMS may be contacted to provide a one-day temporary password that will unlock and re-activate the account.

11.3   RDE Data Entry

11.3.1 The laboratory shall create analytical sets, referred to as Groups in RDE, so that all samples related to the corresponding set's QA Recovery Data, are included under one unique Group identification number. Multiple Groups for the same commodity and month are acceptable.

11.3.2 Matrix Spike Recovery data shall be entered that are associated to all samples in the Group as specified in SOP PDP-QC.

11.3.3 Sample identity information for collected and non-collected samples shall be entered from a paper SIF or attached to the Group if an electronic SIF was submitted. Ensure that the sample identification information match the information that is recorded in RDE.

11.3.4 Analytical Results data shall be entered for each sample as specified in this SOP.

11.3.5 Process Control spike recovery data shall be entered for each sample as specified in SOP PDP-QC.

11.3.6 Data may be entered, maintained, and signed-off on a Laboratory Management Information System (LIMS), but shall be imported into the RDE System for transmission to USDA/AMS.

11.3.7 Refer to the latest RDE System documentation for further information.

11.4   RDE Data Sign-off and Transmission

11.4.1 The data must go through a multi-level review and sign-off process prior to submission to USDA/AMS (the RDE system provides for up to three reviewer sign-offs for each analytical set). The first level sign-off is optional, while the TPM and Quality Assurance Officer sign-offs are required before the analytical set is allowed to be transmitted. A proxy sign-off for the TPM and/or QAO can be done for data sets that are imported from a LIMS provided that the TPM and QAO have both reviewed and approved

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the data. Data may be maintained on a LIMS, but must be transmitted through the web-based RDE system.

11.4.2 Data shall be electronically transmitted to USDA/AMS as described in this SOP using the Transmit option in the RDE System. Analytical data on any other media shall not be submitted without prior authorization from USDA/AMS.

11.4.3 Participating laboratories shall submit electronic results for routine data sets to USDA/AMS via RDE within 90 days of receipt of the last sample in the set according to established procedures as detailed in this SOP. If the 90 day reporting requirement is not met, the laboratory shall send the MPD Director and Laboratory Liaison monthly updates detailing the reason for the delay and a projected schedule for data delivery.

11.4.4 USDA/AMS and the laboratory will come to a written agreement, on a case-by-case basis, regarding any changes to be made to program data after it has been reported to the PDP database. The laboratory shall be responsible for making any changes to hardcopies and their own internal database/records.

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Agricultural Marketing Service, Science & Technology
Pesticide Data Program

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Revision 7	March 2020	Monitoring Programs Division

- Removed reference to the Pesticide Chemical News Guide in section 4 and replaced it with the US Tolerance Tracker
- Renumbered sections 6.2.1 through 6.2.4 so that the sections are now numbered 6.2.2 through 6.2.5
- Added a new section 6.2.1 to provide incurred residue subtraction language for matrix matched standards
- Updated language for reporting a Z code only if LOQ is not entered in section 9.2.1
- Updated language for new name of PCNG service in section 9.5.2
- Updated language for account management in the new local RDE system in section 11.1.1
- Removed italicized note from section 11.1.1 as it does not apply to the local RDE system
- Updated language for account creation in the local RDE system in section 11.1.2
- Updated language for the user management option name in section 11.1.3
- Added section 11.1.4 for updating look-up tables in the local RDE system
- Updated language for system requirements for the local RDE system in section 11.2.1
- Updated language for user access for the local RDE system in section 11.2.2
- Updated language for allowed data sign-off in LIMS in section 11.3.6
- Updated section 11.4.3 by changing the PDP Technical Director to MPD Director and adding notification to the Laboratory Liaison when there is a delay in data delivery

Revision 6	April 2018	Monitoring Programs Division

- Changed GC and LC ion ratio criteria to +/- 30% relative in sections 7.4.1.4 and 7.4.2.3
- Added analyte confirmation language and ion ratio tolerance example calculation to section 7.4.2
- Added electronic data retention requirement to section 8.2.2
- Updated language for PT reporting in section 9.9
- Removed sections 9.9.1 and 9.9.2
- Updated language to address restricted access to RDE in section 11.2.2
- Added new codes for determinative method to Attachment 1

Revision 5	April 2017	Monitoring Programs Division

- Added multipeak confirmation criteria to section 7.4.2.1
- Clarified sample identity information in section 11.3.3

Revision 4	February 2016	Monitoring Programs Division

- Updated language for quantification of multi-peak compounds in section 6.4
- Updated language for quantification of spikes in section 6.5
- Changed GC and LC retention time criteria to 0.1 minutes in section 7.2

- Clarified tolerances for metabolites are based on parent levels in section 9.5

Revision 3	November 2014	Monitoring Programs Division

- Updated MPD address
- Updated procedures for method validation package submission to section 8.2.3
- Updated PDP Tolerance Table procedures to section 9.5
- Updated RDE System Access procedures to section 11.2
- Added new codes for determinative method, extraction, and test class to Attachment 1

Revision 2	August 2013	Monitoring Programs Division

- Updated MPO to USDA/AMS throughout document
- Changed requirement for calibration integrity to 30% for residues not detected in routine samples in sections 6.13 and 7.1.1
- Clarified reporting exceptions in section 6.5
- Added requirement for name/initials/signature log to section 8.1.4

Revision 1	April 2011	Monitoring Programs Office

- Added paragraph regarding sample dilution in section 6.2.4.
- Added specification about incurred residues in section 6.5.3.
- Added sections 6.5.5-6.5.8 regarding spike coding in RDE.
- Updated section 7.1.1 for redundant information.
- Changed "shall" with "should" in section 7.3.2 to reflect MPO needs.
- Updated section 7.4.2.3.
- Updated section 9.1.1 by taking out "best two out of three" requirement.
- Updated section 9.8.4 with relevant pesticide example.
- Updated Attachments 1 and 2 with QA Codes

Original Revision	April 2010	Monitoring Programs Office

- Combined all PDP DATA (03, 07, 09) and INSTR (04, 06) into a single document as follows:
  - PDP – INSTR 04 is section 7.1
  - PDP – INSTR 06 is section 5 (Instrumentation)
  - PDP – DATA 03 is section 6 (Calibration)
  - PDP – DATA 07 is spread over sections 8 (Data Handling), 9 (Data Reporting), 10 (Data Review) and 11 (RDE System)
  - PDP – DATA 09 is section 7 (Generating Raw Data)
- Removed requirements to check instruments performance verification before/during analysis from old PDP - INSTR 06, section 5.4.b.

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- Removed requirements to include comment in SIF field when using "E" code, from old PDP – DATA 03, section 5.1.c.1, currently section 9.2.9.
- Moved and reworded section 5.1.c from old PDP – DATA 03 to chapter 9 (Data Reporting), section 9.2.9 of current PDP – DATA.
- Updated section 5.3.b from old PDP – DATA 07 (currently section 8.2.2)
- Reworded section 5.5 from old PDP – DATA 07 (currently section 9.3)
- Updated section 5.16.c from old PDP – DATA 07 (currently section 11.4.3)

Pesticide Data Program
Laboratory Information Form Codes

CONFIRMATION CODES

CODE	CONFIRMATORY METHOD (Instrumental method used to confirm analyte identity)
A	GC/AED - Gas Chromatography with Atomic Emission Detector
C	GC or LC Alternate Column
CD	GC or LC Alternate Column and Alternate Detector
D	GC or LC Alternate Detector
F	Liquid Chromatography with Fluorescence Detector
GF	GC/TOF - Gas Chromatography with Time of Flight Mass Spectrometry
GI	GC/MS/MS - Gas Chromatography with Tandem Mass Spectrometry - ion trap
GN	GC/MSD w/ Negative Chemical Ionization (NCI)
GT	GC/MS/MS - Gas Chromatography with Tandem Mass Spectrometry - triple quadrupole
HR	GC or LC High Resolution Mass Spectrometry
I	GC/IT - Gas Chromatography with Ion Trap Mass Spectrometry - single stage
IA	Immunoassay
LF	LC/TOF - Liquid Chromatography with Time of Flight Mass Spectrometry
LI	LC/MS - Liquid Chromatography with Ion Trap Mass Spectrometry - single stage
LL	LC/MS/MS - Liquid Chromatography with Tandem Mass Spectrometry - ion trap
LS	LC/MS - Liquid Chromatography with Mass Spectrometry - single quadrupole
LU	LC/MS/MS - Liquid Chromatography with Tandem Mass Spectrometry - triple quadrupole
M	GC/MS - Gas Chromatography with Mass Spectrometry - single quadrupole
MO	Quantitation & Confirmation by GC/MS only
MR	GC or LC Mid Resolution Mass Spectrometry
P	LC-AMP - Liquid Chromatography Alternate Mobile Phase
R	LC-DAD - Liquid Chromatography with Diode Array Detector
S	GC or LC -MS Alternate Detector (see PDP-Data-03.5.7)
Z	Other

ANNOTATION CODES

CODE	ANNOTATED INFORMATION (Additional information about analyte finding)
Q	Residue at Below Quantifiable Level (BQL)
QV	Residue at <BQL> with a Presumptive Violation - No Tolerance
QX	Residue at <BQL> with a Presumptive Violation - Exceeds Tolerance
V	Residue with a Presumptive Violation - No Tolerance
X	Residue with a Presumptive Violation - Exceeds Tolerance

QUANTITATION CODES

CODE	QUANTITATION (Method used to calibrate, quantitate or validate analyte)
(none/blank)	No qualifications of data or non-detect
E	Estimate
P	Marginal performing analyte
U	Unvalidated compound

MEAN RESULT CODES

CODE	MEAN RESULT (Summary of analyte findings and how they were determined)
O	Detect: original extraction value
R	Detect : re-extraction analysis value
A	Detect: average of original and re-extraction analyses values
ND	Non-detect: validated, well-recovered analyte
NP	Non-detect: marginal performing analyte
NU	Non-detect: unvalidated residue
M	Not analyzed (not in standard, used as a marker only)
UD	Unable to determine (matrix interference, method failure)

QA/QC Codes (Exception Codes)

CODE	QA/QC RESULT (Summary of spike recoveries)
I	Incurred residue when levels>2xLOQ
N	Not recovered
S	Incurred subtracted
E	Estimate
M	Matrix interference
P	Marginal performing analyte
U	Unvalidated

Pesticide Data Program
Laboratory Information Form Codes

	DETERMINATIVE CODES	
CODE	**DETERMINATIVE METHOD** (Instrumental method used to quantitate analyte)	

CODE	DETERMINATIVE METHOD
01	GC/ECD - Electron Capture Detector
02	GC/FPD - Flame Photometric Detector in Phosphorus Mode
03	GC/FPD - Flame Photometric Detector in Sulfur Mode
04	GC/ELCD - Electrolytic Conductivity Detector in Nitrogen Mode
05	GC/ELCD - Electrolytic Conductivity Detector in Halogen Mode
06	GC/FID - Flame Ionization Detector
07	GC/MS - Gas Chromatography with Mass Spectrometry - single quadrupole
08	GC/IT - Gas Chromatography with Ion Trap Mass Spectrometry - single stage
09	TLC - Thin Layer Chromatography
10	LC/FL - Liquid Chromatography with Fluorescence Detector
11	LC/UV - Liquid Chromatography with UV Detector
12	Liquid Chromatography with Post-Column Derivatization & Fluorescence Detection
14	GC/NPD - Phosphorus Mode
15	GC/NPD - Nitrogen Mode
16	GC/NPD - Nitrogen/Phosphorus Detector
18	GC/FPD - Flame Photometric Detector in Nitrogen Mode
19	Liquid Chromatography with Pre-Column Derivatization & Fluorescence Detection
27	GC/AED - Atomic Emission Detector
28	AED - Element Selective GC/AED
30	GC/ELCD - Electrolytic Conductivity Detector in Sulfur Mode
35	GC/MS/MS - Gas Chromatography with Tandem Mass Spectrometry - triple quadrupole
51	LC/MS - Liquid Chromatography with Mass Spectrometry - single quadrupole
52	LC/MS/MS - Liquid Chromatography with Tandem Mass Spectrometry - triple quadrupole
58	GC - Gas Chromatography w/ Detector other than Listed
59	LC - Liquid Chromatography w/ Detector other than Listed
60	GC/XSD - Halogen Specific Detector
63	Second LC/MS
64	Second LC/MS/MS
65	GC/Micro ECD - Micro Electron Capture Detector
66	GC/PFPD - Pulsed Flame Photometric Detector
67	Third LC/MS/MS
68	Second GC/ECD
70	Fourth LC/MS/MS
71	Second GC/Micro ECD
72	GC/MSD with Negative Chemical Ionization (NCI)
73	GC/MS/MS - Gas Chromatography with Tandem Mass Spectrometry - ion trap
74	LC/MS - Liquid Chromatography with Ion Trap Mass Spectrometry - single stage
75	LC/MS/MS - Liquid Chromatography with Tandem Mass Spectrometry - ion trap
76	GC/TOF - Gas Chromatography with Time of Flight Mass Spectrometry
77	LC/TOF - Liquid Chromatography with Time of Flight Mass Spectrometry
78	Second GC/MS - single quadrupole
79	GC/HRMS-Gas Chromatography with High Resolution Mass Spectrometry
80	LC/HRMS-Liquid Chrmatography with High Resolution Mass Spectrometry
98	Immunoassay Screen
99	OTHER

Pesticide Data Program
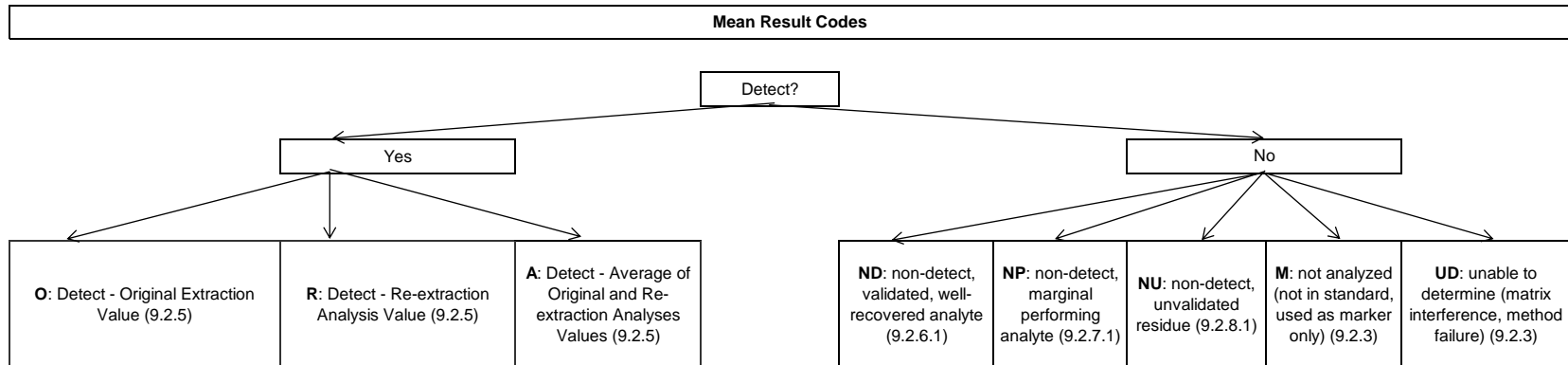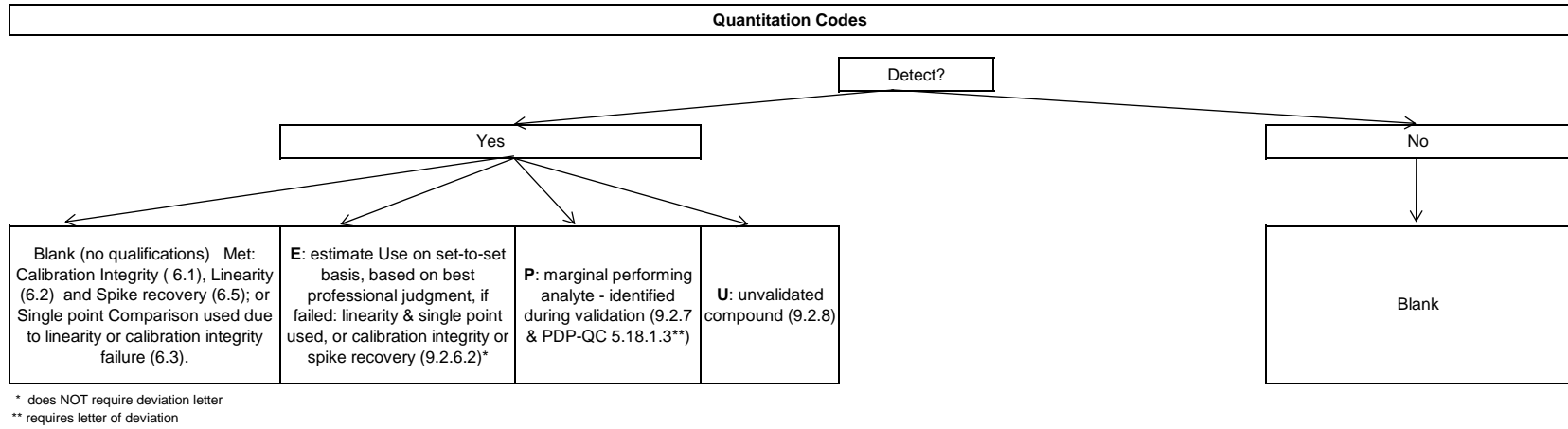## Laboratory Information Form Codes

EXTRACTION CODES	
CODE	**EXTRACTION METHOD** (Extraction method used for this analyte)
000	No Extraction Necessary
015	Modified Luke Extraction Method without Cleanup for Multi-Residues & Carbamates
550	CDFA Lee et al C-18 Extraction Method
551	CDFA Chlorinated ACN Florisil SPE Extraction Method
552	CDFA MSD Aminopropyl Extraction Method
553	CDFA Carbamate SPE Extraction Method
554	CDFA Organophosphate Florisil SPE Extraction Method
555	CDFA Chlorinated Aminopropyl SPE Extraction Method
556	CDFA LC compounds Florisil SPE Extraction Method
800	FL-Modified CDFA C-18 Extraction Method (P-fraction)
801	FL-Modified CDFA C-18 Extraction Method Aminopropyl SPE Cleanup
802	FL-Modified CDFA C-18 Extraction Method w/ Florisil SPE Cleanup
803	GIPSA Modifed Method for Extraction of Multi-Residues in Grains
804	GIPSA Modified Method for Determination of Triazole Metabolites in Wheat Flour (SPE, LC/MS-MS)
805	Modified Quecher's Method
806	NYS Modifed SPE Method (F&V)
807	NYS Modified Method for Determination of Triazoles and Metabolites in Peaches (SPE, LC/MS-MS)
808	WSDA Modified Method for Determination of Triazoles and Metabolites in Apples (SPE, LC/MS-MS)
809	NSL Butter Extraction Method
810	Montana SPE Triazole Extraction Method for Water
811	Montana SPE Extraction Method for Polar Pesticides (Water)
812	Montana Liquid/Liquid Extraction Method for Non-Polar Pesticides
813	NSL Dairy Product Method
814	WA-Modified CDFA C-18 Extraction Method (P-fraction)
815	WA-Modified CDFA C-18 Extraction Method Aminopropyl SPE Cleanup
816	WA-Modified CDFA C-18 Extraction Method w/Florisil SPE Cleanup
817	FL Aminopropyl SPE Extraction Method
818	NSL Animal Tissue Extraction Method
819	EPA Extraction Method
820	Phenoxy Extraction Method
821	NSL Honey Extraction Method
822	CDFA-Modified QuEChERS Method
823	WSDA Animal Tissue Extraction Method
900	Liquid/Liquid Method
901	NYS Modification of USGS Method 2001/2002 (SPE, GC)
902	NYS Modification of USGS Method 9060 (SPE, LC)
903	NYS Modification of USGS Method for Chloroacetanilide Metabolites (SPE, LC)
997	OTHER Methods Used for Determination of Single Components
998	OTHER Single-Analysis Methods
999	OTHER Multi-Residue Methods

Pesticide Data Program
Laboratory Information Form Codes

TEST CLASS CODES	
CODE	TEST CLASS (Test classifications for analytes)
A	Halogenated
B	Benzimidazole
C	Organophosphorus
D	Avermectin
E	Carbamate
F	Organonitrogen
G	2,4-D / Acid Herbicides
H	Formetanate HCL
I	Other Compounds
J	Imidazolinone
K	Sulfonyl Urea Herbicides
L	Conazoles / Triazoles
M	Dithiocarbamates
N	Imidazoles
O	Pyrethroids
P	Thiocarbamates
Q	QA only (for RDE)
R	Triazines
S	Triazine, Non-Halogenated
T	Nitrile
U	Uracil
V	Pyrimidone
W	Morpholine
X	Natural Pesticides
Z	LOD equals LOQ (for RDE)

1) Sample Results (LIF Codes)

Quantitation Codes

Detect?

Yes | No

Blank (no qualifications) Met: Calibration Integrity (6.1), Linearity (6.2) and Spike recovery (6.5); or Single point Comparison used due to linearity or calibration integrity failure (6.3).	**E**: estimate Use on set-to-set basis, based on best professional judgment, if failed: linearity & single point used, or calibration integrity or spike recovery (9.2.6.2)*	**P**: marginal performing analyte - identified during validation (9.2.7 & PDP-QC 5.18.1.3**)	**U**: unvalidated compound (9.2.8)	Blank

 * does NOT require deviation letter
** requires letter of deviation

Mean Result Codes

Detect?

Yes | No

O: Detect - Original Extraction Value (9.2.5)	**R**: Detect - Re-extraction Analysis Value (9.2.5)	**A**: Detect - Average of Original and Re-extraction Analyses Values (9.2.5)	**ND**: non-detect, validated, well-recovered analyte (9.2.6.1)	**NP**: non-detect, marginal performing analyte (9.2.7.1)	**NU**: non-detect, unvalidated residue (9.2.8.1)	**M**: not analyzed (not in standard, used as marker only) (9.2.3)	**UD**: unable to determine (matrix interference, method failure) (9.2.3)

2) QA/QC Results (QA/QC Codes)
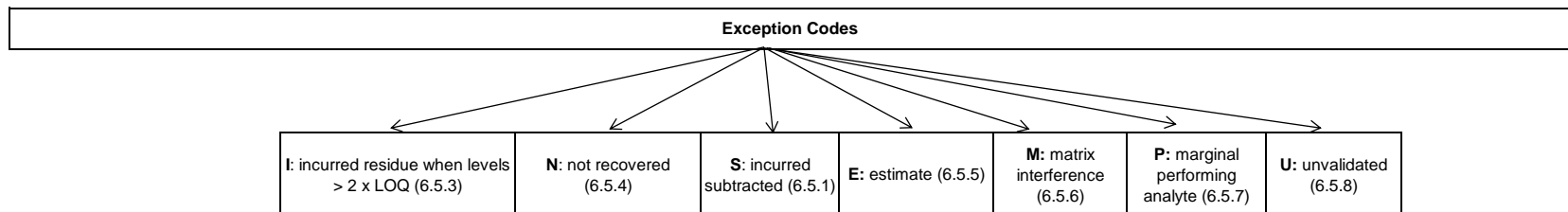
Exception Codes

I: incurred residue when levels > 2 x LOQ (6.5.3)	**N**: not recovered (6.5.4)	**S**: incurred subtracted (6.5.1)	**E**: estimate (6.5.5)	**M**: matrix interference (6.5.6)	**P**: marginal performing analyte (6.5.7)	**U**: unvalidated (6.5.8)

Adduct ion: Ion formed by the interaction of the molecular ion and another compound or element (e.g., ammonium, hydrogen, sodium, etc.) as a result of van der Waals forces.

Atmospheric pressure chemical ionization (APCI): Ionization process where an aerosol of sample solution is sprayed at atmospheric pressure into a heated region creating a reaction between a reagent ion and a neutral molecule to create a charged ionic form of the molecule.

Atmospheric pressure ionization (API): Ionization process carried out at atmospheric pressure by any of several procedures including a radioactive source, electrical discharges, light sources, and high voltage electric fields. The main types are APCI, APPI, and ESI.

Atmospheric pressure photo ionization (APPI): Ionization process where an aerosol of sample solution is sprayed at atmospheric pressure into an area with a light source creating a reaction between photons and a neutral molecule to create a charged ionic form of the molecule.

Atomic mass unit (amu): An arbitrarily defined unit in terms of which the masses of individual atoms are expressed. One amu is exactly 1/12 of the mass of an atom of the nuclide ^{12}C (the predominant isotope of carbon).

Base peak: The ion with the most intense peak in the mass spectrum (full scan). The relative abundance of the base peak is assigned a value of 100%, and the abundance of all other ions plotted in that reference spectrum are normalized to that value.

Chemical ionization (CI): Ionization process initiated by the reaction of a reagent ion and a neutral molecule to create a charged ionic form of the molecule.

Collision induced dissociation (CID): Process by which an isolated ion is fragmented, producing an MS/MS spectrum. CID is sometimes called collision activated dissociation.

Confidence limits: The upper and lower boundaries in the range of values which includes (with a pre-assigned probability called the confidence level) the true value of a parameter.

> "Absolute" confidence limits: Confidence limits determined for relative abundances of structurally significant ions by adding ± the pre-assigned confidence level. For example, an absolute confidence limit of 15%, for ion 149 with a relative abundance of 45%, the confidence interval would be 30% to 60%.

> "Relative" confidence limits: Confidence limits determined for relative abundances of structurally significant ions by multiplying ± the pre-assigned confidence level. For example, a relative confidence limit of 15% for ion 149 with a relative abundance of 45%, the confidence interval would be 38% [45×(100-15)/100] to 52% [45×(100+15)/100].

United States Department of Agriculture
Agricultural Marketing Service, Science & Technology
Pesticide Data Program
Glossary of Mass Spectrometry Terms and Acronyms

Confirmation: Verification of a previous analyte identification that is performed by another analytical system.

Deconvolution: Process to extract clean spectra from a complex mixture of overlapping peaks using mathematical algorithms.

Diagnostic ion(s): Ion(s) used to identify and quantitate the target compound. Diagnostic ions include the molecular ion, characteristic adduct ions, characteristic fragment ions (structurally significant ions), and isotope ions.

Electron ionization (EI): Ionization process initiated by the interaction of the gas-phase molecule with an energetic electron to create a charged ionic form of the molecule. Electron ionization is sometimes called electron impact.

Electrospray ionization (ESI): Ionization process where a sample solution is pumped into a capillary which is held at high potential causing a reaction between a reagent ion and a neutral molecule to create a charged ionic form of the molecule. The solution emerges from the capillary as a mist which is sprayed at atmospheric pressure into the mass spectrometer.

Fragment ion(s): Ion(s) formed when the precursor or product ion fractures after undergoing CID. All fragment ion(s) are product ion(s), but not all product ion(s) are fragment ion(s)

Full scan: The practice of monitoring and recording a wide range of ion mass-to-charge ratios (m/z) produced following sample ionization.

Ion trap: Type of mass analyzer consisting of two end caps and a ring electrode forming a three-dimensional quadrupole that stores ions at its center. An additional electrical signal is used to selectively eject ions to an external detector.

Ionspray™ ionization: Pneumatically assisted ESI. Ionspray ionization is also called turbospray ionization.

Internal standard: A substance not contained in the test sample with physical and chemical properties as similar as possible to those of the target analyte to be identified. An isotope-labeled form of the target analyte can also serve as an internal standard. The internal standard is added to each test sample as well as to each calibration standard at the beginning of the analytical process and used in the quantitative determination of the target analyte by taking into account the recovery of the internal standard.

Matrix-assisted laser desorption ionization (MALDI): Ionization process where sample molecules are mixed with an excess of energy-absorbing matrix. The subsequent mixture is co-

crystallized in a thin film on an inert support. Repetitive irradiation with a pulsed laser releases ions from the surface.

Molecular ion: An ion formed by the removal or addition of one or more electrons to a molecule without fragmentation; the peak representing the ionized molecule that contains only the isotopes of greatest natural abundance.

Mass spectrometry (MS): Analytical technique used to identify compounds based on their chemical structures' fragmentation patterns. MS instruments are called mass spectrometers.

Mass spectrometry/mass spectrometry (MS/MS): A form of mass spectrometry whereby ions are separated according to their mass-to-charge ratio in the first stage and are then fragmented by collisionally-induced dissociation, and the resultant fragment ions separated and measured in the second stage. MS/MS is also referred to as tandem mass spectrometry.

MS^n: MS/MS reactions recurring over multiple steps.

MS spectrum: Graphical representation of ion intensity vs. m/z data at a single point in time.

MS/MS spectrum: Graphical representation of ion intensity vs. m/z data at a single point in time produced by an isolated mass undergoing CID.

Multiple reaction monitoring: Selected reaction monitoring for more than one precursor-to-product ion transition.

m/z: A ratio of mass-to-charge.

Precursor ion: An abundant, structurally significant ion selected from the full scan spectrum to be isolated and subsequently subjected to CID. A precursor ion may be a molecular ion or a fragment ion. The precursor ion is sometimes called the parent ion.

Precursor ion scan: The practice of using the second stage mass analyzer in an MS/MS experiment to select a specific product ion and then using the first stage mass analyzer to scan for the precursor ion(s). The term parent ion scan is also used.

Product ion(s): Ion(s) formed from the reaction of the precursor ion. The reaction need not involve fragmentation through CID (e.g., the reaction involves a change in the number of charges carried by the precursor ion). If the reaction does involve CID, the product ion is also a fragment ion. Product ion(s) are sometimes called daughter ion(s).

Product ion scan: The practice of using the first stage mass analyzer in an MS/MS experiment to select a specific precursor ion and then using the second stage mass analyzer to scan for the resulting product ions. The term daughter ion scan is also used.

Quadrupole: Type of mass analyzer consisting of four parallel rods arranged in a square array. Radio frequency and direct current voltages are applied to the rods creating a hyperbolic field that filters ions based on their mass-to-charge ratio.

Qualifier ion(s): Structurally significant ion(s) chosen from the reference spectrum to show consistent relative abundances when compared to the target ion. Qualifier ion(s) are sometimes called secondary ion(s).

Quantitation ion: A structurally significant ion that demonstrates a linear response over a broad range of concentrations. It is typically the target ion.

Reconstructed ion chromatogram: A plot of the intensity of specific ions in a MS or MS/MS spectrum (based on m/z) versus time.

Reference spectrum: Graphical representation of ion intensity vs. m/z data at a single point in time.

Relative abundance: The abundance of an ion relative to that of the most abundant ion, or base peak, in the spectrum.

Selected ion monitoring (SIM): Data acquisition technique of monitoring and recording one or more ion mass-to-charge ratios (m/z) rather than monitoring and recording the full MS spectra (i.e., a wide range of m/z values). This technique can greatly improve instrument sensitivity, albeit at a cost of reduced specificity. The term single ion monitoring is sometimes used.

Selected reaction monitoring (SRM): The MS/MS techniques of monitoring and recording one or more precursor-to-product ion transitions rather than monitoring and recording the full MS/MS spectra (i.e., all precursor or product ions). This practice can serve to greatly increase signal-to-noise by reducing noise.

 "Soft" ionization: Low energy ionization process that typically results in little or no molecule fragmentation. The ions are usually either protonated $(M+H)^+$ or deprotonated $(M-H)^-$. Soft ionization processes include (but are not limited to) CI, ESI, APCI, and APPI.

Structurally significant ion: Ion with a mass-to-charge ratio (m/z) which indicates a characteristic structural grouping formed by the fragmentation of a molecule.

Target ion: A structurally significant ion selected from the reference spectrum, typically the most abundant ion, to be used to generate relative abundance ratios with qualifier ions. The target ion is sometimes called the primary ion.

Time-of-flight (TOF) mass analyzer: Type of mass analyzer that uses the flight time of an ion over a fixed distance to measure its mass. Lower mass ions will move through fixed distance faster than higher mass ions.

Total ion current: A plot of the summed intensity of all acquired ions in a MS or MS/MS spectrum versus time. The term total ion chromatogram is also used.