

**United States Department of Agriculture  
Agricultural Marketing Service, Science and Technology  
Pesticide Data Program**

SOP No.: PDP-QC-07		Page 1 of 17
Title: Demonstration of Method Performance		
Revision: 5	Replaces: 07/01/03	Effective: 07/01/04

**1. Purpose:**

To provide USDA/AMS Pesticide Data Program (PDP) a mechanism by which to evaluate a laboratory's ongoing ability to perform analyses when there are additions/changes in pesticides or commodities or analytical methods.

**2. Scope:**

This standard operating procedure (SOP) shall be followed by all analytical laboratories that have completed the applicable PDP-QC-02, "Initial Laboratory Evaluation", and are conducting stability or other types of studies that may impact the program.

**3. Definitions:**

Refer to Glossary

**4. Outline of Procedures:**

- 7.1 Evaluation Guidelines
- 7.2 Analytes/Commodities/Methods
- 7.3 Establishment of Estimated LODs and LOQs
- 7.4 Verification of LODs
- 7.5 LOD Check
- 7.6 Determination of Consistent Instrumental Response
- 7.7 Determination of Method Performance
- 7.8 Precision and Accuracy Data Collection
- 7.9 Method Evaluation Reporting

Attachment 1 – Method Evaluation Flowchart, July 1, 2004

Attachment 2 – Method Evaluation Reporting Forms [Verification of Limits of Detection (LODs), LOD Check, Determination of Consistent Instrumental Response, Determination of Method Performance, Precision and Accuracy Data Collection], July 1, 2004

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**5. References:**

- USDA/AMS PDP Quality Assurance/Technical Meeting, May 18-20, 2004, Fairfax, VA
- USDA/AMS PDP Quality Assurance/Technical Meeting, May 7-9, 2003, Manassas, VA
- USDA/AMS PDP Quality Assurance/Technical Meeting, April 9-11, 2002, Manassas, VA
- USDA/AMS PDP Quality Assurance/Technical Meeting, February 21-22, 2001, Tallahassee, FL
- Chemist Qualification document from Robert Epstein and summarized by Terry Jackson with State participant comments, April 23, 1992
- Validation of Methods Used in the Florida Department of Agriculture and Consumer Services' Chemical Residue Laboratory, Parker, G.A., JAOAC, 74, No. 5, pp. 868-871, 1991
- Quality Assurance Principles for Analytical Laboratories, Garfield, F., AOAC, 1991
- Quality Assurance of Chemical Measurements, Taylor, J.T., Lewis Publishers, 1989
- Evaluation of Analytical Methods Used for Regulation of Foods and Drugs, Horwitz, W., Analytical Chemistry, Vol. 54, No. 1, pp. 67A-76A, 1982

**6. Historical Background and Philosophical Overview:**

At the start of the Pesticide Data Program, it was recognized that the methods used for analysis must be validated. The problem encountered was the enormous number of combinations of pesticides and commodities the participating laboratories were asked to screen. To help make this a manageable task, two concepts were invented: marker compounds, and commodity groups. Each concept seeks to group pesticides or commodities by common properties and exploits these common properties to reduce the possible combinations to a manageable number. These concepts were introduced in PDP-QC-07 and PDP-QC-02 with mixed results. The interaction of these two SOPs and these two concepts has been marked with considerable confusion. In an effort to reduce the confusion associated with these two SOPs, PDP-QC-02 was archived July 1, 2004.

For PDP-QC-07, two additional concepts are introduced: modules and scenarios. These concepts are outlined in section 7.1. This allows for the systematic and logical application of

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method evaluation requirements (modules) to several commonly encountered situations (scenarios) in the PDP laboratories while exploiting the properties of marker compounds and commodity groups.

It is assumed that problems will lead to an investigation of causes, such as instrument reproducibility and instrument linearity.

A flow diagram is attached (*see Attachment 1*) which further clarifies these concepts.

**7. Specific Procedures**

7.1 Evaluation Guidelines

7.1.a. After a laboratory has completed Initial Laboratory Evaluation for the marker pesticides, further changes/additions of pesticides, commodities or methods require additional evaluation. The following scenarios of changes/additions are possible:

7.1.a.1 Implementing a new method (7.2.a)

7.1.a.2. Changing an analytical method

7.1.a.2.a Extraction (7.2.b.1)

7.1.a.2.b Post-extraction/pre-instrumentation (7.2.b.2)

7.1.a.2.c Instrumentation

7.1.a.2.c.1. New technology (7.2.b.3.a)

7.1.a.2.c.1.a. New LOD

7.1.a.2.c.1.b. Same (existing) LOD

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7.1.a.2.c.2. Replacement/duplicate (7.2.b.3.b)

7.1.a.2.d. Minor Modifications (7.2.b.4.)

7.1.a.3. Adding a new commodity grouping (7.2.c)

7.1.a.4. Adding a new commodity or a processed commodity to an existing commodity group. (7.2.d)

7.1.a.5. Adding pesticides related to marker pesticide groups to an existing commodity group. (7.2.e) *(see PDP-QC-13 for listing of commodity grouping and marker pesticide groups and applicable PDP-QC-13 addenda for required pesticides)*

7.1.a.6. Adding a new pesticide that is not related to marker pesticide groups to an existing commodity group. (7.2.f)

7.1.b Evaluation takes place through the performance of method evaluation modules. These modules are chosen to meet the requirements of each scenario. The seven modules are:

1. Establishment of Estimated LODs and LOQs according to PDP-QC-10 (7.3)
2. Verification of LODs (7.4)
3. LOD Check (7.5)
4. Determination of Consistent Instrumental Response. (7.6)
5. Determination of Method Performance over a range of levels (from 1xLOQ to 10xLOQ). (7.7)
6. Determination of Method Precision and Accuracy at 2xLOQ. (7.8)
7. Method Evaluation Reporting. (7.9)

7.1.c. Section 7.2 of this SOP lists each scenario and the modules that must be performed in that scenario. Sections 7.3 through 7.9 outline the detailed procedures to be followed for each module.

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7.1.d. This method evaluation framework makes the following assumptions:

- 7.1.d.1 Commodities are grouped in such a way that assessment of method performance in one commodity in the group can be extended to apply to all commodities in the group.
- 7.1.d.2. Marker pesticides are chosen to be representative of a broad range of similar pesticides. The assessment of method performance for these pesticides can be extended to apply to similar pesticides.
- 7.1.d.3. A method can be evaluated using representative commodities and marker pesticides. Once a method is evaluated for these pesticides, it can be extended to other commodities and pesticides.
- 7.1.d.4. LOD is specific to a pesticide and must be evaluated for every pesticide.
- 7.1.d.5. Although a method may be extended to other commodities and pesticides, a minimum amount of recovery data must be obtained to confirm this assumption.

7.2 Analytes/Commodities/Methods (*see PDP-QC-13 for PDP commodity groupings and marker pesticide groups and applicable PDP-QC-13 addenda for required pesticides*). The Technical Program Manager and Quality Assurance Officer will determine which scenario described in the following subsections applies. If local agreement cannot be reached, the PDP Technical Director shall be contacted to determine which modules should be performed.

7.2.a. *New method implementation*: The most difficult to analyze commodity currently analyzed by the laboratory in each group shall be selected for each applicable section.

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*Proceed with*

- Establishment of Estimated LODs and LOQs (7.3)
- Verification of LODs/LOQs for all compounds (7.4)
- Determination of Consistent Instrumental Response for all compounds (7.6)
- Determination of Method Performance for marker compounds (7.7)
- Precision and Accuracy Data Collection for all compounds (7.8)
- Method Evaluation Reporting (7.9)

7.2.b. *Method changes*: The most difficult to analyze commodity currently analyzed by the laboratory in each group shall be selected for each applicable section.

7.2.b.1. Major Extraction Change - Examples would be using a different solvent or a new technique such as microwave extraction or supercritical fluid extraction.

*Proceed with*

- Establishment of Estimated LODs and LOQs (7.3)
- Verification of LODs/LOQs for all compounds (7.4)
- Determination of Consistent Instrumental Response for all compounds (7.6)
- Determination of Method Performance for marker compounds (7.7)
- Precision and Accuracy Data Collection for all compounds (7.8)
- Method Evaluation Reporting (7.9)

7.2.b.2. Major changes in post-extraction/pre-instrumentation procedures. (Cleanup).

*Proceed with*

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- Verification of LODs/LOQs for all compounds (7.4)
- Determination of Consistent Instrumental Response for all compounds (7.6)
- Determination of Method Performance for marker compounds (7.7)
- Precision and Accuracy Data Collection for all compounds (7.8)
- Method Evaluation Reporting (7.9)

7.2.b.3. Instrumentation Changes

7.2.b.3.a. New technology

7.2.b.3.a.1 New LOD

*Proceed with*

- Establishment of Estimated LODs/LOQs for all compounds (7.3)
- Verification of LODs/LOQs for all compounds (7.4)
- Determination of Consistent Instrumental Response for all compounds (7.6)
- Precision and Accuracy Data Collection for all compounds (7.8)
- Method Evaluation Reporting (7.9)

7.2.b.3.a.2. Same (existing) LOD

*Proceed with*

- LOD Check (7.5.a)
  - Determination of Consistent Instrumental Response for all compounds (7.6)
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- Precision and Accuracy Data Collection for all compounds (7.8)
- Method Evaluation Reporting (7.9)

7.2.b.3.b. Replacement/duplicate

*Proceed with*

- LOD Check (7.5.b)
- Determination of Consistent Instrumental Response for all compounds (7.6)
- Method Evaluation Reporting (7.9)

7.2.b.4. Minor modifications of existing method: The approval process for modifications is defined in SOP PDP-QC-05.

The Technical Program Manager and Quality Assurance Officer will determine which portions of the following sections will be completed. *This is dependent upon the extent of modification. If local agreement cannot be reached, the PDP Technical Director shall be contacted to determine which sections should be performed.*

*Proceed with*

- Establishment of Estimated LODs and LOQs (7.3)
- Verification of LODs and LOQs (7.4)
- Determination of Consistent Instrumental Response (7.6)
- Determination of Method Performance (7.7)
- Precision and Accuracy Data Collection (7.8)
- Method Evaluation Reporting (7.9)

7.2.c. Adding a new commodity group:

*Proceed with*

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- Verification of established LODs/LOQs for all required pesticides in the new commodity (7.4)
- Determination of Method Performance for the marker pesticides (7.7)
- Precision and Accuracy Data Collection for all required analytes (7.8)
- Method Evaluation Reporting (7.9)

7.2.d. Adding a commodity or a processed commodity to an existing commodity group:

*Proceed with*

- Verification of established LODs/LOQs for all required pesticides (7.4)
- Precision and Accuracy Data Collection (2 points) for all required pesticides (7.8)
- Method Evaluation Reporting (7.9)

7.2.e. Adding pesticides related to the marker pesticide groups to an existing commodity group: The new analyte(s) will be evaluated for the most difficult to analyze commodity currently analyzed by the laboratory in each group.

*Proceed with*

- Establishment of Estimated LODs and LOQs for each pesticide added (7.3)
- Verification of LODs/LOQs for each pesticide added (7.4)
- Determination of Consistent Instrumental Response (7.6)
- Precision and Accuracy Data Collection for each pesticide added (7.8)
- Method Evaluation Reporting (7.9)

7.2.f. Adding pesticides that are not related to the marker pesticide groups to an existing commodity group. (For example, the addition of imidacloprid analyzed by the same multiresidue procedure. The new pesticide may then become a marker pesticide for similar pesticides that are later added.)

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*Proceed with*

- Establishment of Estimated LODs and LOQs for each pesticide added (7.3)
- Verification of LODs and LOQs for each pesticide added (7.4)
- Determination of Consistent Instrumental Response for each pesticide added (7.6)
- Determination of Method Performance for compound(s) that are to become marker(s) (7.7)
- Precision and Accuracy Data Collection for each pesticide added (7.8)
- Method Evaluation Reporting (7.9)

7.3 Establishment of Estimated LODs and LOQs

7.3.a. See SOP PDP-QC-10, Estimation of LOD and LOQ for Chromatographic Methods.

7.4 Verification of LODs and LOQs

7.4.a. All calculated or established LODs must be verified by fortifying duplicate blank commodities at approximately the LOD level and subjecting them to the analytical method.

7.4.b. Verification consists of the observation of detectable peaks in the chromatogram at three times the current noise level (run within the last three months). Variability is expected to be high. Therefore, recoveries can be reported as present or not present. If detectable peaks are not observed, the LOD must be re-estimated and the verification repeated.

7.4.c. Prepare summary form(s) of the acquired data (*see Attachment 2*).

7.5 LOD Check

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- 7.5.a. The LOD for each reported compound shall be checked, at least yearly, by extraction of an LOD spike.
  - 7.5.b. The sensitivity shall be checked when instrument systems change (e.g, new instruments and/or detector) by injecting an LOD standard.
  - 7.5.c. LODs may be raised for analytes in an individual sample set at the discretion of Technical Program Manager.
  - 7.5.d. LODs may not be lowered without verification subject to the analytical method, Technical Program Manager approval, and QA review.
  - 7.5.e. All LOD check data generated shall be maintained and housed by the QAU.
  - 7.5.f. Prepare summary form(s) of the acquired data (*see Attachment 2*).
  - 7.6 Determination of Consistent Instrumental Response
    - 7.6.a. Standards containing the analytes specified in section 7.2 shall provide consistent responses at levels equivalent to LOQ, 5xLOQ and 10xLOQ on the primary injector and detector system. If additional injector and detector combinations are to be used for quantification, they must be likewise evaluated.
    - 7.6.b. **Standards in Matrix:** Choose a representative commodity. For each analyte specified in section 7.2, run a three point standard curve (at a minimum) from LOQ to 10xLOQ. This curve is run three times over three days for a minimum of nine points.
    - 7.6.c. **Standards Not in Matrix:** For each analyte specified in section 7.2, run a three point standard curve (at a minimum) from LOQ to 10xLOQ. This curve is run three times over three days for a minimum of nine points.
    - 7.6.d. Calculate appropriate fitness of curve parameter (refer to PDP-DATA-03) for each of the three days.
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- 7.6.e. Prepare summary form(s) of the acquired data (*see Attachment 2*).
- 7.6.f. If the calibration range is extended to quantitate results outside of the normal calibration range, enter the appropriate information in the “Curve Extended” columns on the Consistent Instrumental Response summary form (*see Attachment 2*).

7.7 Determination of Method Performance

- 7.7.a. Fortified samples are to be run through the entire analytical method on the primary injector and detector system. If additional injector and detector combinations are to be used for quantification, they must be likewise evaluated.
  - 7.7.b. Fortify samples in triplicate at approximately LOQ, 5xLOQ, and 10xLOQ for each marker or single analysis PDP analyte in the most difficult to analyze commodity currently analyzed by the laboratory. Process these fortified samples through the entire analytical method (treat as a set of nine samples). A reagent and matrix blank shall be subjected to the analytical method along with the fortified analytes.
  - 7.7.c. For each data point, calculate the Percent Recovery compared to known standards to 3 significant figures if greater than 100% or to two significant figures if less than 100%.
  - 7.7.d. Calculate the Coefficient of Variation (%CV) for each level. A definition of Horwitz expected intralaboratory and interlaboratory %CVs may be found in SOP PDP-Glossary. The appropriate values may be used as a guideline when evaluating data.
  - 7.7.e. Prepare summary form(s) of the acquired data (7.7.c and d) by analyte, level, and commodity group (*see Attachment 2*). Refer to SOP PDP-QC-04 for PDP acceptance criteria of this acquired data.
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7.8 Precision and Accuracy Data Collection

7.8.a. The precision and accuracy data collection shall be compiled from the commodity groupings as specified by USDA/AMS. Each marker, single analysis, new or other required PDP analyte as specified in section 7.2 shall be spiked at 2xLOQ and evaluated using a minimum of seven data points, with at least two points from each commodity in the group.

7.8.b. The required data points shall be obtained from:

7.8.b.1. 2xLOQ data points completed after Determination of Method Performance.

and/or

7.8.b.2. Data points from matrix spikes analyzed concurrently with samples.

These two options provide slightly different data. The second option is preferable since it provides information about the repeatability of the method over time. The first option is permitted when running concurrent spikes would extend the data collection over more than 6 months and/or concurrent spikes would make the size of sample sets unmanageable.

7.8.c. For each data point, calculate the Percent Recovery compared to known standards to 3 significant figures if greater than 100% or to two significant figures if less than 100%.

7.8.d. Calculate the Coefficient of Variation (%CV) for each pesticide using the seven data points. A definition of Horwitz expected intralaboratory and interlaboratory %CVs may be found in SOP PDP-Glossary. The appropriate values may be used as a guideline when evaluating data.



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7.8.e. Prepare summary form(s) of the acquired data (*see Attachment 2*). Refer to SOP PDP-QC-04 for PDP acceptance criteria.

7.9 Method Evaluation Reporting

7.9.a. The methodology, method evaluation records, summary form(s), and any other raw data generated during PDP-QC-07 evaluation shall be maintained by the QAU.

7.9.b. Once the laboratory has completed:

- Verification of LODs and LOQs (7.4)
- LOD Check (7.5)
- Determination of Consistent Instrumental Response (7.6)
- Determination of Method Performance (7.7)
- Precision and Accuracy Data Collection (7.8)

The summary form(s) and a brief narrative describing the method and results should be sent to the PDP Technical Director together with a cover memo detailing the submission (state which scenario(s) and module(s) that the submission is intended to represent). Submission of complete method evaluation studies is preferred; however, some laboratories have chosen to submit the modules in a piecemeal fashion. If a complete set of modules is not submitted it should be clearly stated.

Example text for a cover memo follows:

Enclosed is the complete method validation summary of compound “x” in commodity “y” supporting the addition of commodity “x” to the 2003-2005 PDP program. The summary documents detail our results of establishment, verification of LOD’s and LOQ’s, LOD check, determination of consistent instrumental response, determination of method performance, and precision and accuracy data collection. If there are questions about this submission please contact: XXXXXX. All references to this submission should use QA# ###-####.

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An example format for the submission follows:

Title

Summary to include purpose, results, data anomalies.

Methods

Sample Preparation (example):

50g homogenized sample extracted with 100 ml ACN by gently mixing

5ml extract purified by a C-18 SPE cartridge, eluted with MeOH, and concentrated to 5 mls

1 ml eluate further purified by florisil SPE and eluted with 5 mls 50:50 hexane/acetone

Eluate dried down to 0.5 ml, re-suspended in acetone, and filtered

Derivatization accomplished by reaction with dansyl chloride.

Analysis (example):

Instrument GC/HPLC/detector

Column (DB-)

Post-column derivatization (where applicable).

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*Gail Parker*

*6-16-04*

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Date

*Diana Haynes*

*6-18-04*

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Approved By: Diana Haynes  
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# Method Evaluation Flowchart











