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

SOP No.: PDP-QC-06		Page 1 of 10
Title: Minimum Requirements for GC/Quadrupole Mass Spectrometer Confirmation in EI Mode		
Revision: 4	Replaces: 04/01/00	Effective: 06/01/02

1. Purpose:

To provide uniform minimum requirements for the operation of quadrupole mass spectrometers using electron ionization (EI) mode.

2. Scope:

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

3. Outline of Procedures:

7.1 Apparatus and Materials
7.2 Reference Spectra
7.3 Minimum Requirements for Confirmation of GC/quadrupole mass spectrometer in EI mode
7.4 Documentation

4. Narrative:

This SOP resulted from many discussions aimed at providing minimum control points for QA use while allowing the MS operator to make effective use of the mass spectrometer's capabilities. Numerous concepts were considered including screening, confirmation, tuning, full scan, SIM, isotope clusters, molecular ions, and relative abundances. Accordingly, a set of criteria was developed to help the QAU assure the quality of the mass spectrometry; however, as with any complex system, the criteria cannot cover all possible scenarios and a provision has therefore been added in which a PDP laboratory can ask for an exception to the minimum requirements presented in this SOP.

5. Definitions:

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

Confirmation: Additional identification of an analyte screened by another analytical system.

Molecular ion: The ionized molecule; the peak representing the ionized molecule that contains only the isotopes of greatest natural abundance.

Base peak: The most intense peak in the mass spectrum (full scan), hence 100% relative abundance.

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.

Self-confirmation: The simultaneous identification (based on retention time), quantitation, and confirmation (based on mass spectral data) obtained upon a single injection.

"Absolute" confidence limits: Confidence limits determined for relative abundances of structurally significant ions (7.3.d.3.d) by **adding ± 15%**, e.g., ion 149 with a relative abundance of 45% would have a confidence interval of 30% to 60%.

"Relative" confidence limits: Confidence limits determined for relative abundances of structurally significant ions (7.3.d.3.d) by **multiplying by 85% and 115%,** e.g., ion 149 with a relative abundance of 45% would have a confidence interval of 38% to 52%.

6. References:

- USDA/AMS PDP Quality Assurance (QA)/Technical Meeting, April 9-11, 2002
- USDA/AMS PDP Federal/State Meeting, October 26-28, 1999
- USDA/AMS PDP Quality Assurance Meeting, May 18-20, 1999
- SOP PDP-QC-06 Attachment 1, "Flowchart for Minimum Requirements of Confirmation of GC/Quadrupole Mass Spectrometer in EI Mode"
- USDA/AMS PDP Mass Spectrometry (MS) Work Group Meeting, March 23-24, 1999
- Cairns and Siegmund, Regulatory Pesticide Analysis by Mass Spectrometry, Analytical Methods for Pesticides and Plant Growth Regulators, Vol. IV, pp. 193-253
- USDA/AMS PDP Quality Assurance Committee Meeting, June 10-11, 1997
- Sphon, Use of Mass Spectrometry for confirmation of Animal Drug Residues
- U.S. EPA, 40 CFR 136, parts II, VI, and VIII
- Middleditch and Hines, Mass Spectrometry of Priority Pollutants Hites, Handbook of Mass Spectra of Environmental Contaminants

7. Specific Procedures to be Followed:

These operating procedures provide minimum requirements for a quadrupole GC/mass spectrometer system operated in EI mode for both full scan and selected ion monitoring (SIM) applications and are presented as general procedures. Each participating laboratory shall, as part of their internal laboratory SOPs, have written instructions providing specific details concerning how these procedures have been implemented in that laboratory. Separate SOP documents shall be written for spectra acquired utilizing other modes or systems, e.g., chemical ionization (CI) mode, ion trap detector (ITD), and LC/MS applications.

7.1 Apparatus and Materials

a. Gas Chromatograph/Mass Spectrometer System

1. A temperature programmable gas chromatograph, complete with all accessories and equipped with a quadrupole mass spectrometer.

2. A capillary column, which demonstrates good chromatography.

3. The GC/quadrupole mass spectrometer must be equipped with 70 electron volts energy in the EI mode (high or low resolution), capable of scanning 20-500 atomic mass units (amu). The GC/ quadrupole mass spectrometer system must produce a mass spectrum, which meets all the calibration criteria listed in subsection 7.4 of this SOP. The GC/quadrupole mass spectrometer must have the ability of acquiring m/z abundance data in SIM mode for groups of four or more masses.

4. A computer system shall be interfaced to the GC/quadrupole mass spectrometer that allows it to acquire and store data of all mass spectra obtained throughout the duration of an analysis. The software shall have a library search option of the acquired data.

b. Reagents

1. The mass spectral analysis shall require the use of known standards of the compounds being confirmed. All standard solutions shall be handled according to PDP SOPs.

2. If reagent or matrix broad background interference restricts the sensitivity of the GC/quadrupole mass spectrometer analysis, additional cleanup procedures (e.g., Florisil column, SepPak, etc.) are recommended.

3. Use of internal standards to monitor variability in retention times and sensitivity is suggested but not required. This is especially recommended any time the GC/quadrupole mass spectrometer is used for quantitation.

7.2 Reference Spectra

a. Tune Reference

The tune program provided by the instrument manufacturer shall be used for instrument tuning. The manufacture's specification for DFTPP, PFTBA, or other specified compound shall be used to establish proper instrument tune. A hardcopy of the tune result will be archived for future QA review.

b. Standard Reference

1. Reference spectrum of routine standards is required prior to routine analysis. An injection of the standard, at approximately five times the minimum level of detection is made to generate a standard reference spectrum. The same GC/quadrupole mass spectrometer operating conditions must be used for subsequent sample analysis. This spectrum must be kept on file to serve as a comparison spectrum for future evaluation of the standard. This record will have as a minimum the following information: response, retention time, spectrum, ion abundances normalized to the base peak, date of injection, time of injection, name of GC/quadrupole mass spectrometer operator, parameters under which the injection was made, and parameters of GC/quadrupole mass spectrometer. Note, this reference spectrum is to be updated when it is determined the system has changed due to aging or different operating conditions.

2. Structurally significant ions used for confirmation/identification shall be placed in a table that is included in laboratory SOPs. Note, occasionally ion relative intensities may change because of instrument aging or different operating conditions. In such cases the table is to be updated as necessary.

7.3 Minimum Requirements of Confirmation of GC/Quadrupole Mass Spectrometer in EI Mode

Refer to Attachment 1, "Flowchart for Minimum Requirements of Confirmation of GC/Quadrupole Mass Spectrometer in EI Mode", for summary of requirements.

a. An air/water check shall be generated within four hours prior to the start of a sequence.

b. A tune profile shall be generated within four hours prior to the start of a sequence.

c. A matrix blank shall be analyzed with each set of samples.

d. A residue in the sample is determined by satisfying the following criteria:

1. 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.

2. 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 ± 0.05 minutes.

3. The mass spectrum of the sample component matches the mass spectrum of the standard injected that day under the same conditions. The following paragraphs define the word "match".

a. Structurally significant ions chosen for identification/confirmation must have intensities 3 times noise (refer to PDP-QC-10).

b. The structurally significant ions chosen for confirmation should have molecular weights greater than 91. Other ions of lower m/z may be considered depending on the structural significance.

c. A minimum of three structurally significant ions, meeting condition of $ 3 times noise, are required for identification. If the molecular ion is present at $ 3 times noise, it must be included as one of the three ions.

Note, an isotope cluster may be considered as one Aion@ or one ion out of the isotope cluster may be used to satisfy one of the three ions. In other words, the ions of an isotope cluster are not to satisfy the requirement of three structurally significant ions when other ions are available. Also, the ions of an isotope cluster are not to satisfy the requirement of the three structurally significant ions even when no others are available.

d. Relative abundances of structurally significant ions used for SIM confirmation should agree to "10% (absolute) of the standard of that day. Relative abundances of structurally significant ions used for full scan confirmation should agree to "20% (absolute) of the standard of that day.

e. Dealing with Exceptions - When a compound cannot routinely meet the above criteria due to the nature of the compound or the analytical system, an exception can be requested by the Technical Program Manager and reviewed by the QA officer. The request shall explain the exception and how the confirmation will be accomplished by the GC/quadrupole mass spectrometer. All requests shall be documented and the documentation shall be maintained by the laboratory.

7.4 Documentation

The following documents shall be kept as part of confirmation QA/QC.

a. Chromatograms for air or water as a means to check for an air/water leak.

b. Hard copies of tuning profiles, generated prior to sample analyses, of any compound used for tuning (PFTBA, DFTPP, etc.) as well as logs of all instrument maintenance such as source cleaning, replacement of inserts, septums, and columns.

c. Copies of chromatograms of samples, standards, matrix blanks, and reagent blanks shall be kept with the raw data pack.

d. Hard copies of reference spectra.

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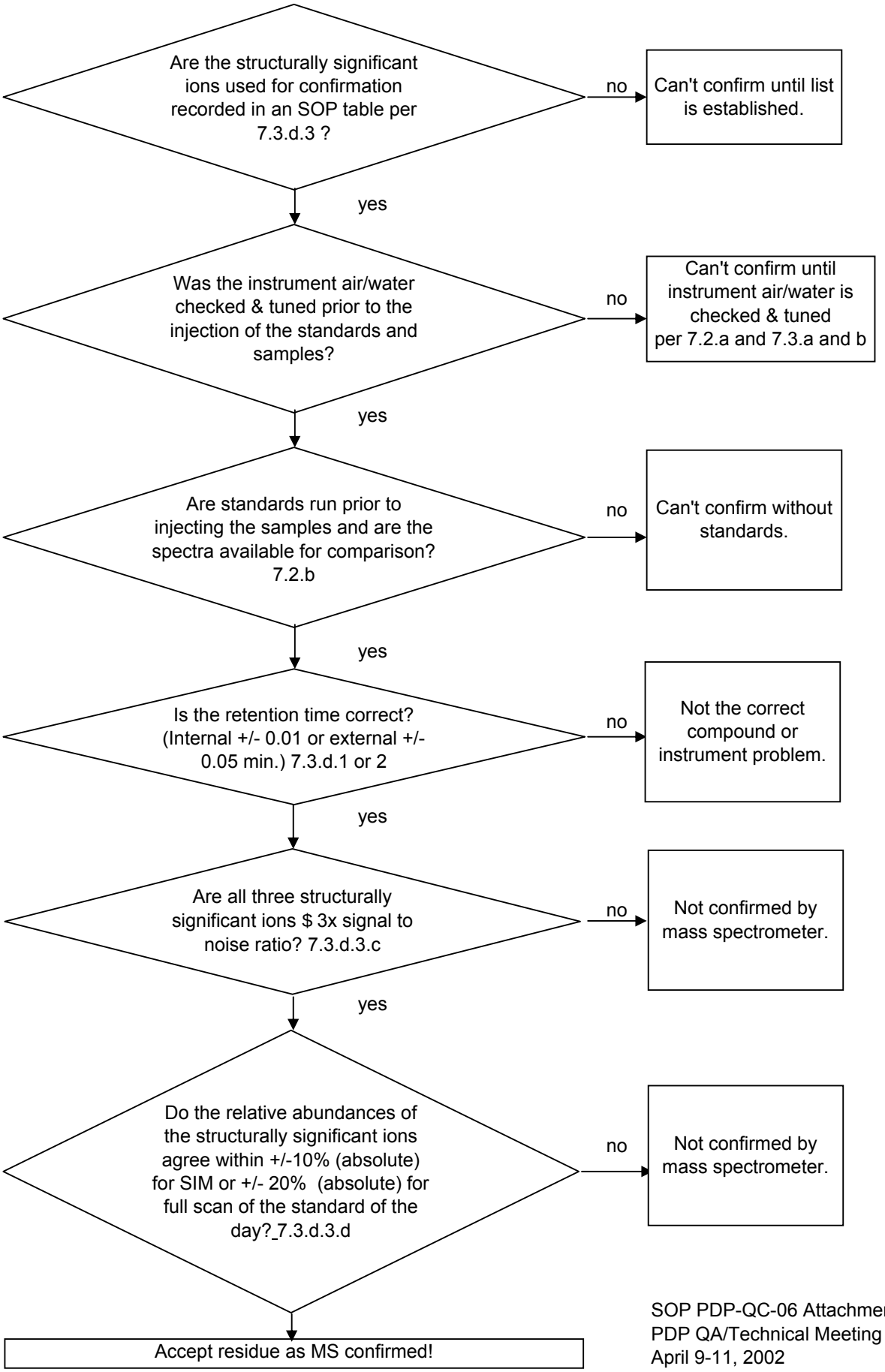
Revision 4 April 2002 PDP QA/Technical Meeting

- Added “absolute” and “relative” confidence limit definitions to section 5
- Updated references in section 6
- Added “selected ion monitoring” to expand on SIM to section 7
- Substituted “an analysis” for “the chromatographic program” in section 7.1.a.4
- Added reference to Attachment in subsection 7.3
- Substituted “+\-” for “within” in section 7.3.d.2
- Added parentheses in section 7.3.d.3
- Corrected format numbering in section 7.4

Flowchart for Minimum Requirements of Confirmation of GC/Quadrupole Mass Spectrometer in EI Mode



SOP PDP-QC-06 Attachment 1, Rev. 01
PDP QA/Technical Meeting
April 9-11, 2002