



Department of Pesticide Regulation



Mary-Ann Warmerdam
Director

MEMORANDUM

Arnold Schwarzenegger
Governor

TO: Randy Segawa
Environmental Program Manager I

Environmental Monitoring Branch

FROM: Wisam M. Fattah
Environmental Scientist
Environmental Monitoring Branch
(916) 324-4191

DATE: August 21, 2008

SUBJECT: DETERMINATION IF THE CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE, CENTER FOR ANALYTICAL CHEMISTRY'S LIQUID CHROMATOGRAPHY-ATMOSPHERIC PRESSURE CHEMICAL IONIZATION MASS SPECTROMETRY METHOD FOR ATRAZINE, BROMACIL, CYANAZINE, DIURON, HEXAZINONE, METRIBUZIN, NORFLURAZON, PROMETON, PROMETRYN, SIMAZINE, DEETHYL ATRAZINE, DEISOPROPYL ATRAZINE, DIAMINO CHLOROTRIAZINE, DES-METHYL NORFLURAZON IN WELL WATER AND RIVER WATER (METHOD EM-62.9), MEETS THE "UNEQUIVOCAL DETECTION" CRITERIA

Background

The Pesticide Contamination Prevention Act (Food and Agriculture Code [FAC] sections 13141 et seq.) was passed in 1985 to prevent further pesticide pollution of ground water which may be used for drinking water supplies. FAC section 13149 specifies the conditions under which a pesticide is considered "found" in ground water or soil, and thus subject to formal review as specified. As originally adopted, FAC subsection 13149(d) specified that a pesticide detection should be verified by a second analytical method or a second analytical laboratory approved by the Department of Pesticide Regulation. However, Senate Bill 810 amended the law in 1995 to allow a finding of a pesticide in ground water or soil to be based on a single analytical method conducted by a single analytical laboratory, if the analytical method provides unequivocal identification of a chemical. Following this change, general criteria were established to identify methods providing unequivocal identification of a chemical (Biermann, 1996).

Issue

Does the California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry's liquid chromatography-mass spectrometry (LC-MS) method EM-62.9 (Tran et al., 1999), revised in 2007 for the addition of desmethyl norflurazon, meet the definition of an "unequivocal detection" method?



Discussion and Recommendation

CDFA method EM-62.9 uses a high performance liquid chromatograph coupled to a chemical ionization/ion trap mass spectrometer. Prior to injection of sample into the LC-MS apparatus, the well and river water samples are cleaned and extracted using solid phase extraction. Consequently the well and river water samples generally contain a minimal amount of background/matrix interference, facilitating the goal of unequivocal detection.

In CDFA method EM-62.9 3 criteria are used to confirm the presence of the 15 herbicides:

1. The high performance liquid chromatograph separates each compound according to its characteristic retention time (RT), where the RT is required to be within two percent of that observed with authentic standard.
2. A mass spectrometric scan for molecular species with mass/charge values equivalent to each analyte's parent or molecular ion takes place at the specified RT window.
3. A mass spectrometric scan for an ion mass range corresponding to each analyte's characteristic fragment or product ion(s) also takes place at the specified RT window.

Based on the above criteria of method EM-62.9, if a particular analyte elutes in the specified RT window, and the correct parent ion appears during the specified RT window, and the correct product ion(s) appear during the specified RT window, then that analyte has been identified in the sample. To summarize, each analyte in the sample is identified by characteristic RT, the presence of a parent molecular ion and the presence of at least one daughter fragment ion. Consequently, analysis of the 15 herbicides by method EM-62.9 qualifies for the unequivocal detection designation.

APPROVED: Original Signed by _____ Date: 03/23/2010
John S. Sanders, Ph.D.
Environmental Program Manager II

APPROVED: Original Signed by Lisa Ross for _____ Date: 03/22/2010
Randy Segawa
Environmental Program Manager I

Randy Segawa
August 21, 2008
Page 3

References

Biermann, H., 1996. Memorandum to K. Goh, "Definition of 'unequivocal detection methods' for the purposes of Senate Bill 810."

Tran, Duc and Pamela Fitch, 1999. Method of analysis by the California Department of Food and Agriculture, Center for Analytical Chemistry—Determination of atrazine, bromacil, cyanazine, diuron, hexazinone, metribuzin, norflurazon, prometon, prometryn, simazine, deethyl atrazine (DEA), deisopropyl atrazine (ACET), diamino chlorotriazine (DACT), des-methyl norflurazon in well water and river water by liquid chromatography-atmospheric pressure chemical ionization mass spectrometry. Method EM-62.9.