



# 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

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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 TEBUTHIURON AND ITS DEGRADATES<sup>1</sup> 104, 106, 107, AND 108 IN WELL WATER (METHOD EM-SM-05-005), MEETS THE "UNEQUIVOCAL DETECTION" CRITERIA

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### 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-SM-05-005 (Lee, 2007) for tebuthiuron and its degradates 104, 106, 107, and 108, meet the definition of an "unequivocal detection" method?

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<sup>1</sup>Degradates' 104, 106, 107 and 108 chemical names, respectively: N-[5-(1,1-Dimethylethyl)-1,3,4-thiadiazol-2-yl]-N-methylurea, N-[5-(1,1-Dimethylethyl)-1,3,4-thiadiazol-2-yl]-urea, 2-Dimethylethyl-5-methylamino-1,3,4-thiadiazol, 2-Dimethylethyl-5-amino-1,3,4-thiadiazole.



## **Discussion and Recommendation**

### *Tebuthiuron and degradates 104, 106, 107, and 108*

CDFA method EM-SM-05-005 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 water samples are cleaned and extracted using solid phase extraction. Consequently the well water samples generally contain a minimal amount of background/matrix interference, facilitating the goal of unequivocal detection.

In CDFA method EM-SM-05-005 three criteria are used to confirm the presence of tebuthiuron and each of its four degradates:

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-SM-05-005, if a particular analyte elutes at  $\pm$  two percent of the standard's RT, 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 unequivocally identified in the sample. Consequently, analysis of tebuthiuron and its degradates by this method qualifies for the unequivocal detection designation.

### *Degradates 104 and 107*

Any time that multiple analyte samples are analyzed via LC-MS, the potential for co-elution exists. In the case of CDFA method EM-SM-05-005, tebuthiuron degradates 104 and 107 co-elute within one-hundredth of one second of each other (0.01 seconds) preventing unique identification and quantitation. To resolve this matter, a second analysis is conducted where the

Randy Segawa  
August 21, 2008  
Page 3

LC mobile phase composition is altered (see CDFA method EM-SM-05-005, Section 4, "Interferences") allowing distinct separation of the two degradates, followed by unequivocal MS detection as described above.

APPROVED: Original Signed by  
John S. Sanders, Ph.D.  
Environmental Program Manager II

Date: 03/23/2010

APPROVED: Original Signed by Lisa Ross for  
Randy Segawa  
Environmental Program Manager I

Date: 03/22/2010

Randy Segawa  
August 21, 2008  
Page 4

## **References**

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

Lee, Paul, 2007. Method of analysis by the California Department of Food and Agriculture, Center for Analytical Chemistry—Determination of tebuthiuron and its degradates 104, 106, 107, and 108 in well water by liquid chromatography-atmospheric pressure chemical ionization mass spectrometry. Method EM-SM-05-005.