



MEMORANDUM

TO: Carissa Ganapathy
Senior Environmental Scientist
Environmental Monitoring Branch

FROM: Vaneet Aggarwal, Ph.D. Original signed 2/21/2020
Environmental Scientist
916-445-3870

DATE: February 21, 2020

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-041 AS UNEQUIVOCAL
ACCORDING TO CRITERIA IN THE PESTICIDE CONTAMINATION
PREVENTION ACT

BACKGROUND

The Pesticide Contamination Prevention Act (Food and Agricultural Code [FAC] sections 13141 et seq.) was passed in 1985 to prevent further pesticide pollution of groundwater which may be used for drinking water supplies. FAC section 13149 specifies the conditions under which a pesticide is considered “found” in groundwater or soil, and thus subject to formal review as specified. FAC subsection 13149(d) allows a finding of a pesticide in groundwater or soil to be based on a single analytical method conducted by a single analytical laboratory, only if the analytical method provides unequivocal identification of a chemical. The criteria and discussion of DPR’s process for qualifying methods that provide unequivocal identification of a chemical are included in the memo entitled “Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act requirements” (Aggarwal, 2012). The memo describes that a method is deemed unequivocal if it meets specific selectivity and/or structural analysis criteria. This qualification memo serves to establish if the method EMON-SM-05-041 meets those criteria.

PURPOSE

Determine if the analytical method (EMON-SM-05-041) for Sulfentrazone and Sulfentrazone-3-Carboxylic Acid in well water used by the California Department of Food and Agriculture (CDFA) meets the definition of an unequivocal method.

DISCUSSION AND RECOMMENDATION

The CDFA Center for Analytical Chemistry method EMON-SM-05-041 uses a Liquid Chromatography coupled to a Linear Ion Trap Quadrupole LC/MS/MS for the detection of Sulfentrazone and its metabolite (Sulfentrazone-3-Carboxylic Acid) in well water. Prior to the injection of a sample into the LC/MS/MS, a measured volume of groundwater sample (250 mL) is acidified with hydrochloric acid (HCl) and passed through a Water’s Oasis® Weak Anion-

eXchange (WAX) cartridge. The analytes are then eluted with 5% ammonium hydroxide in methanol and the eluant is concentrated to ~ 0.3 mL. The eluant is then brought up to a final volume of 2 mL by first adjusting the volume to 1 mL with water followed by the addition of 1 mL of acetonitrile. The extract is then analyzed by LC/MS/MS.

A method is considered “unequivocal” based on (a) matching retention time of the certified reference standard, (b) presence of the precursor ion at the retention time, and/or (c) presence of one or more characteristic product ions (Aggarwal, 2012). In method EMON-SM-05-041, the first quadrupole in the mass spectrometer is set to reject all species with mass/charge values that do not correspond to the analyte’s ammonium adduct ion eluting at that analyte’s particular retention time. Each ammonium adduct ion is then fragmented in the next stage and the third quadrupole in the mass spectrometer quantifies the pesticides based on either one or two characteristic fragments. Therefore, this method uses three stepwise factors to eliminate possible interferences for these pesticides: chromatographic retention times, molecular ion masses, and specific product ion masses.

As specifically stated in method EMON-SM-05-041, the following criteria are used to confirm the presence of Sulfentrazone and Sulfentrazone-3-Carboxylic Acid in well water:

1. For positive results, the retention time shall not vary from standards by more than ± 0.1 minute.
2. Presence of both qualification and quantification ion.

Analysis of Sulfentrazone and Sulfentrazone-3-Carboxylic Acid by method EMON-SM-05-041 is highly specific and qualifies for unequivocal detection designation. Therefore, analysis by a second laboratory or a second method is not necessary for well water samples analyzed for Sulfentrazone and Sulfentrazone-3-Carboxylic Acid using this method.

APPROVED: Original Signed by
Carissa Ganapathy
Senior Environmental Scientist

Date: 2/21/2020

APPROVED: Original Signed by
Joy Dias
Environmental Program Manager I

Date: 2/21/2020

Carissa Ganapathy
February 21, 2020
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APPROVED: Original Signed by
Edgar Vidrio,
Environmental Program Manager II

Date: 2/21/2020

REFERENCES

Aggarwal, V. 2012. Memorandum to Lisa Ross, Ph.D. Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act requirements. Available at: https://www.cdpr.ca.gov/docs/emon/grndwtr/polprocd/pcpa_requirements_analytical_methods_compliance.pdf (accessed 19 February 2020).