

Department of Pesticide Regulation

Gavin Newsom

Yana Garcia Secretary for Environmental Protection

MEMORANDUM

TO: Joy Dias

Environmental Program Manager I

FROM: Vaneet Aggarwal

Original Signed by

Senior Environmental Scientist

916-445-3870

DATE: July 28, 2025

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-032 REVISION 5

(DRAFT) AS UNEQUIVOCAL ACCORDING TO THE PESTICIDE CONTAMINATION PREVENTION ACT – **INTERIM MEMORANDUM**

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 that may be used for drinking water supplies. FAC section 13149 specifies the conditions under which a pesticide or degradate is considered detected in groundwater, and thus subject to formal review as specified. FAC subsection 13149(d) allows a finding of a pesticide or degradate in groundwater to be based on a single analytical method conducted by a single analytical laboratory if the analytical method approved by the Department of Pesticide Regulation (DPR) provides unequivocal identification of a chemical. DPR's process for qualifying methods that provide unequivocal identification of a chemical is 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 factors. This qualification memo serves to establish if the method EMON-SM-05-032 REVISION 5 (CDFA, 2025) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the draft version of the analytical method EMON-SM-05-032 REVISION 5 (CDFA, 2025) for 70 pesticides in groundwater 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-05-032 REVISION 5 (CDFA, 2025) uses either a liquid chromatography coupled to a tandem mass spectrometer (LC/MS/MS) system, or a gas chromatography coupled to a tandem mass spectrometer (GC/MS/MS) system for the detection of 70 pesticides and degradates in groundwater. LC/MS/MS is used for the determination of 55 pesticides and degradates (Table 1), while GC/MS/MS is used for the detection of 15 pesticides (Table 2). Prior to injection of a sample into the LC/MS/MS or GC/MS/MS apparatus, the analytes are extracted from the groundwater sample (~1 L) with methylene chloride. Two surrogates; atrazine-d₅ and imidacloprid-d₄ are used to verify extraction efficiency.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-032 REVISION 5.

AIBA	Mefenoxam
Atrazine	Methiocarb
Atrazine-d₅ (surrogate)	Methomyl
Azinphos-methyl	Methoxyfenozide
Azoxystrobin	Metolachlor
Bensulide	Metribuzin
Bentazon	Myclobutanil
Bromacil	Napropamide
Carbaryl	Norflurazon
Carbofuran	Oryzalin
Chlorantraniliprole	Phorate Sulfone
Cyantraniliprole	Phorate Sulfoxide
Cyprodinil	Piperonyl Butoxide
Diazinon	Prometon
Dimethenamide	Propanil
Dimethoate	Propiconazole
Dimethomorph	Pyraclostrobin
Diuron	Saflufenacil
Ethofumesate	Simazine
Ethoprophos	Sulfentrazone
Fenamiphos	Sulfentrazone DMS
Fludioxonil	Sulfentrazone Methyl
Flupyradifurone	Tebufenozide
Flutriafol	Tebuthiuron
Imidacloprid	Thiamethoxam
Imidacloprid-d ₄	Thiobencarb
(surrogate)	
Isoxaben	Uniconazole
Linuron	

Table 2. Pesticides determined by GC/MS/MS in CDFA Method EMON-SM-05-032 REVISION 5.

Alachlor	Malathion
Benfluralin	Parathion Ethyl
Clomazone	Parathion Methyl
Dichlobenil	Pendimethalin
Dichloran	Phorate
Disulfoton	Prometryn
EPTC	Triallate
Fonofos	

A method is considered "unequivocal" based on

- (a) matching retention time of the certified reference standard,
- (b) the presence of the precursor ion at the retention time, and/or
- (c) the presence of one or more characteristic product ions (Aggarwal, 2012).

For the above mentioned 70 pesticides and degradates listed in Tables 1 and 2, the method EMON-SM-05-032 REVISION 5 (CDFA, 2025) uses a triple quadrupole mass spectrometer in the multiple reaction monitoring (MRM) mode for quantification. Monitoring for each target analyte occurs in a window surrounding the compound's retention time following chromatographic separation. Retention times are confirmed via certified reference standards. The first quadrupole in the mass spectrometer filters precursor ions with selected mass-to-charge ratios corresponding to the analytes' molecular ion. Each precursor ion is then fragmented in the next stage. Finally, the third quadrupole in the mass spectrometer filters for characteristic fragment ions of the target analytes. Fragment ions are used for quantification and confirmation of each species. Therefore, this method uses four stepwise factors to eliminate possible interferences for these pesticides: chromatographic retention times, molecular ion masses, specific product ion masses, and product ion ratios.

NOTE: The lower control limit (LCL) for AIBA, oryzalin, and sulfometuron methyl during method validation was below 50%. Compounds with LCLs under 50% are classified as marginal. However, identification of these compounds in groundwater using method EMON-SM-05-032 REVISION 5 (CDFA, 2025) is highly specific and meets the criteria for unequivocal identification.

As specifically stated in method EMON-SM-05-032 REVISION 5 (CDFA, 2025), the presence of 70 pesticides and degradates in groundwater are confirmed by:

- 1. The retention time of the analyte is within ± 0.1 minutes of each analyte within the same sequence.
- 2. The relative abundances of structurally significant ions used for confirmation are within ± 30% when compared to a standard injected during the same run.

Identification for these 70 pesticides and degradates in groundwater by method EMON-SM-05-032 REVISION 5 (CDFA, 2025) is highly specific and qualifies as an unequivocal method. Therefore, confirmation by a second laboratory or use of a second method is not necessary for groundwater samples analyzed for these 70 pesticides and degradates by this method.

APPROVED: Original Signed by Date: 7/31/25

Joy Dias

Environmental Program Manager I

APPROVED: Original Signed by Date: 7/31/25

Maziar Kandelous

Environmental Program Manager II (Acting)

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/wp-content/uploads/2024/11/pcpa requirements analytical methods compliance.pd f (accessed June 10, 2025).

CDFA. 2025. EMON-SM-05-032 REVISION 5. Determination of 70 Pesticides in Groundwater by Liquid Chromatography Tandem Mass Spectrometry and Gas Chromatography Tandem Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.