



MEMORANDUM

TO: Joy Dias
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Original Signed by 5/23/23

DATE: May 16, 2023

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-032 REVISION 3 AS
UNEQUIVOCAL ACCORDING TO 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 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 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 3 (CDFA, 2023) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method EMON-SM-05-032 Revision 3 (CDFA, 2023) for 62 pesticides and degradates in groundwater used by the California Department of Food and Agriculture (CDFA) meets the definition of an unequivocal method.

DISCUSSION AND RECOMMENDATION

The CDFCA Center for Analytical Chemistry method EMON-SM-05-032 Revision 3 (CDFCA, 2023) 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 62 pesticides and degradates in groundwater. LC/MS/MS is used for the determination of 46 pesticides and degradates (Table 1), while GC/MS/MS is used for the

detection of 16 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 with methylene chloride. Two surrogates; atrazine-d5 and imidacloprid-d4 are used to verify extraction efficiency.

Table 1. Pesticides or degradates determined by LC/MS/MS in CDEFA Method EMON-SM-05-032 Revision 3.

3,4-Dichloroaniline	Flutriafol
3,5-Dichloroaniline	Imidacloprid
AIBA	Imidacloprid-d4 (surrogate)
Alachlor	Isoxaben
Atrazine	Linuron
Atrazine-d5 (surrogate)	Mefenoxam
Azinphos- methyl	Methiocarb
Azoxystrobin	Methomyl
Bensulide	Methoxyfenozide
Bentazon	Metolachlor
Bromacil	Metribuzin
Carbaryl	Myclobutanil
Carbofuran	Napropamide
Chlorantraniliprole	Norflurazon
Cyprodinil	Oryzalin
Diazinon	Prometon
Dimethenamide	Propiconazole
Dimethoate	Pyraclostrobin
Diuron	Simazine
Ethofumesate	Tebuthiuron
Fenamiphos	Thiamethoxam
Fludioxonil NH4	Thiobencarb
Flupyradifurone	Uniconazole-p

Table 2. Pesticides determined by GC/MS/MS in CDFA Method EMON-SM-05-032 Revision 3.

Benfluralin	Malathion
Clomazone	Parathion Ethyl
Dichlobenil	Parathion Methyl
Dichloran	Phorate
Disulfoton	Piperonyl Butoxide
EPTC	Prometryn
Ethoprophos	Propanil
Fonofos	Triallate

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).

In method EMON-SM-05-032 revision 3 (CDFA, 2023) for the above mentioned 62 pesticides, 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 molecular ion eluting at that analyte’s particular retention time. Each molecular ion is then fragmented in the next stage, and finally 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-05-032 Revision 3 (CDFA, 2023), the presence of 62 pesticides and degradates in groundwater are confirmed by:

1. The retention time of the analyte within ± 0.1 minute of that analyte in the standards within the same sequence.
2. The relative abundance of structurally significant ions used for confirmation within $\pm 30\%$ when compared to a standard injected during the same run.

Identification for these 62 pesticides in groundwater by method EMON-SM-05-032 Revision 3 (CDFA, 2023) 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 the 62 pesticides and degradates by this method.

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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 April 24, 2023).

CDFA. 2023. EMON-SM-05-032 Revision 3. Determination of 62 Pesticides in Groundwater by Liquid Chromatography Tandem Mass Spectrometry and Gas Chromatography Tandem Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.