



MEMORANDUM

TO: Carissa Ganapathy
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Original Signed by 4/6/22

DATE: April 06, 2022

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-032 REVISION 2 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 is considered detected in groundwater, 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, 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 2 is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method (EMON-SM-05-032 revision 2) for 53 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 2 uses either a liquid chromatography coupled to a tandem quadrupole mass spectrometer (LC/MS/MS) system, or a gas chromatography coupled to triple quadrupole mass spectrometer (GC/MS/MS) system for the detection of 53 pesticides in well water. LC/MS/MS is used for the determination of 39 pesticides (Table 1), while GC/MS/MS is used for the detection of 14 pesticides (Table 2). Prior

to injection of sample into the LC/MS/MS or GC/MS/MS apparatus, the pesticides are extracted from the well water sample with methylene chloride.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-032 revision 2.

Alachlor	Isoxaben
Atrazine	Linuron
Azinphos- methyl	Mefenoxam
Azoxystrobin	Methiocarb
Bensulide	Methomyl
Bentazon	Methoxyfenozide
Bromacil	Metolachlor
Carbaryl	Metribuzin
Carbofuran	Napropamide
Chlorantraniliprole	Norflurazon
Cyprodinil	Oryzalin
Diazinon	Prometon
Dimethenamide	Propiconazole
Dimethoate	Pyraclostrobin
Diuron	Simazine
Ethofumesate NH4	Tebuthiuron
Fenamiphos	Thiamethoxam
Fludioxonil NH4	Thiobencarb
Flutriafol	Uniconazole-p
Imidacloprid	

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

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

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-05-032 revision 2 for the above mentioned 53 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 2, the presence of 53 pesticides in groundwater are confirmed by:

1. The retention time of the analyte should be within ± 0.1 minute of the analyte in the standards in the same sequence.
2. Presence of both precursor and product ion. The relative abundances of qualifier ions must be within $\pm 30\%$ relative when compared to a standard injected during the same run.

Analysis of these 53 pesticides by method EMON-SM-05-032 revision 2 is highly specific and qualifies as an unequivocal method. Therefore, analysis by a second laboratory or a second method is not necessary for groundwater samples analyzed for these 53 pesticides by this method.

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April 6, 2022
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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 February 28, 2022).