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SUBJECT: DETERMINATION IF CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE'S AZOXYSTROBIN, AZOXYSTROBIN ACID, AZOXYSTROBIN Z-METABOLITE, DICLORAN, IPRODIONE, ISOIPRODIONE, VINCLOZALIN AND 3,5-DICHLOROANILINE METHOD (EMON-SM-05-018) MEETS THE "UNEQUIVOCAL DETECTION" CRITERIA

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 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 finding of a pesticide shall be verified by a second analytical method or a second analytical laboratory approved by the Department of Pesticide Regulation (DPR). However, the law was amended by Senate Bill 810 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, criteria were established to identify methods providing unequivocal identification of a chemical in a February 13, 1996, DPR memo entitled "Definition of unequivocal detection method for the purposes of Senate Bill 810 (Biermann, 1996)."

ISSUE

Does the analytical method for azoxystrobin, dicloran, iprodione, isoiprodione, Vinclozalin, 3, 5-dichloroaniline, and their degradation products used by the California Department of Food and Agriculture (CDFA) meet the definition of an unequivocal detection method?

DISCUSSION AND RECOMMENDATION

CDFA Center for Analytical Chemistry, Environmental Analysis Section (method EMON-SM-05-018) uses an LC/MS/MS system for the detection of fungicide azoxystrobin and its degradation products, azoxystrobin acid, and azoxystrobin Z-metabolite. For azoxystrobin and the degradates analysis, the first 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 the final mass spectrometer quantifies the fungicide or degradate based on either one or two characteristic fragments. Three stepwise factors are used to eliminate possible interferences for each analyte: chromatographic retention time, analyte molecular ion mass, and either one or two specific daughter ion masses depending on the analyte. Therefore, analysis of the azoxystrobin by this method is highly specific and qualifies for the designation as unequivocal. Therefore, analysis by a second laboratory or a second method is not necessary for well water samples analyzed for azoxystrobin or degradates.

CDFA Center for Analytical Chemistry, Environmental Analysis Section (method EMON-SM-05-018) also uses a GC/MS system for the detection of pesticides, dicloran, iprodione, isoiprodione, and 3, 5-dichloroaniline. For the analysis of each of these chemicals, the mass spectrometer is set to scan for only those species with (i) mass/charge (m/z) values that correspond to analyte's characteristic quantitation ion, and (ii) m/z value(s) that correspond to either one or two confirmation ions for each analyte. These scans occur at the elution time of the analyte. An additional requirement for the analysis to be considered confirmed is that the ratio of the relative integrated abundance of the molecular ion and the confirmation ion must be within ± 20 percent of the ratio observed using known standard. Two stepwise factors are therefore used to eliminate possible interferences for each chemical: chromatographic retention time and two characteristic masses (molecular ion and confirmation ion) for each analyte. The additional requirement that the relative abundance ratio of the characteristic ions is equivalent to that obtained using authentic standard in the absence of known interferents provides a high degree of specificity. Consequently, analysis of the dicloran, and 3, 5-dichloroaniline by this method qualifies for the designation as unequivocal.

Isoiprodione and iprodione are structural isomers that co-elute in this GCMS method. CDFA chemists think that isoiprodione arises from rearrangement of iprodione in the injector and/or on-column, but the mechanism is not fully understood at this time. As a result, there is the potential for confounding of isoiprodione and iprodione if both are present in an environmental sample. For this reason the current method does not qualify for the designation of unequivocal for isoiprodione / iprodione. Information in the literature indicates that the alcohol used for extraction might be a cause of this arrangement (Anisuzzaman et al., 2008). Exploration of different alcohols, such as tert-butanol, that do not degrade iprodione is an option to explore in the future when we revisit this analytical method.

CDFA storage stability data show that 60%-90% of vinclozolin degradates within two days of storage (Appendix 3 and 5). The method validation data yield mean recoveries < 80%. Due to the instability of vinclozolin and typical sample storage durations, we do not feel confident in the detection of vinclozolin. In the future, should we decide monitoring is needed; we will develop a process to stabilize vinclozolin to allow for typical sample storage and analysis procedures. At that time, we will reanalyze the method to see if vinclozolin qualifies for the designation of unequivocal detection.

In summary, CDFA analytical method qualifies for the designation as unequivocal for azoxystrobin, dicloran, 3, 5-dichloroaniline, and their degradation products. However, the current method does not qualify for the designation of unequivocal for the iprodione / isoiprodione, and needs additional method development before a decision can be made for vinclozalin.

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