PMSD/ISB

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Subject: Followup to the Naled Registration Standard; Review of Method Validation Report for Chevron Chemical Co.'s Method RM-3G-4 with Addendum (Determination of Naled and DDVP Residues in Crops, MRID No. 405064-01), 12/1/89

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A method validation was requested in a followup to the Naled Registration Standard (fly and mosquito use, review of 4/5/88, Debra Edwards) for Chevron Chemical Company method RM-3G-4, "Determination of Naled and DDVP Residues in Crops". Analytical Chemistry Section, Chemical Operations Branch, Benefits and Use Division, has submitted the final method validation report "Validation of Naled Method RM-3G-4 With Addendum", dated 12/1/89.

CONCLUSIONS

The analytical method RM-3G-4 with addendum is adequate for enforcement purposes in the subject crop matrices. Since the tolerance expression is written for the combined residues of naled and its metabolite DDVP (calculated as equivalents of naled), the question of conversion of naled to DDVP during the analysis becomes

moot.

RECOMMENDATIONS

The registrant should submit a revised version of method RM-3G-4 which eliminates the recommendation for a particular brand of acetonitrile, and the testing of this solvent to determine whether it converts excessive amounts of naled to DDVP. In addition, the registrant should clearly state that the calculation of residue levels is to reflect the total residues of naled and its metabolite DDVP (calculated as equivalents of naled).

BACKGROUND

In the followup to the Naled Registration Standard, Chevron Chemical Co. submitted a revision of the method currently included in the PAM, Vol. II as enforcement method I (RM-3G, incorrectly cited as RM-3). Neither RM-3G nor its current revision, RM-3G-4 with Addendum, has previously undergone an EPA method validation in crop, i.e., plant matrices. RM-3G has undergone a successful FDA method validation on milk in conjunction with PP#1F1111, at fortification levels of 0.01 and 0.05 ppm.

The current study required a validation of method RM-3G-4 with Addendum for naled and DDVP on almonds (0.5, 1.0 ppm), broccoli (1.0, 2.0 ppm), oranges (3.0, 6.0 ppm), and alfalfa (10.0, 20.0 ppm).

Briefly, the samples are extracted with acidic hexane and filtered through sodium sulfate. An aliquot is taken for partitioning into acetonitrile. The extracts are evaporated and redissolved in water, and the residue partitioned into hexane. The extracts are reduced to a suitable volume and the residues determined by gas chromatography (NP detector). Naled and DDVP appear as two separate peaks for quantitation, DDVP being calculated as equivalents of naled.

ACS/ACB/BUD concluded that method RM-3G-4 with Addendum is not an acceptable regulatory method for naled on almonds, broccoli, oranges, and alfalfa for the following reasons:

1. Conversion of naled to DDVP is much greater than the 5% as reported by Chevron.

2. The method requires the use of a specified brand of acetonitrile.

3. The method requires the use of particular batches of a specified brand of acetonitrile.

ACS noted that a set of three samples may be run in two days if a GC equipped with an autosampler is available. The EPA laboratory also made the following modifications in the subject method:

> "The method specifies a sample weight of 100 grams, but, due to the limited capacity of our centrifuge bottles and the bulk of the ground alfalfa, we used half the volume of the specified extraction solvents and the following sample weights:
>
> | | |
> |---|---|
> | Almonds | 50 grams |
> | Broccoli | 25 grams |
> | Oranges | 25 grams |
> | Alfalfa | 5 grams |

The registrant claims a detection limit of 0.01 ppm. ACS could not obtain this low a detection limit, possibly because smaller sample sizes were used. The none detectable levels for the subject commodities were as follows: almonds <0.03 ppm, broccoli <0.10 ppm, oranges <0.20 ppm, and alfalfa <0.90 ppm.

DISCUSSION

The following table lists the recoveries of naled obtained in the various crop matrices. The recoveries are calculated for residues of naled, per se, and residues of naled and DDVP (calculated as equivalents of naled). All controls contained no detectable residues.

COMMODITY	FORTIFICATION PPM	% RECOVERY NALED	% RECOVERY NALED+DDVP
Almonds	0.50	62, 54	86, 84
	1.00	65, 57	91, 83
Broccoli	1.00	66, 62	85, 84
	2.00	80, 80	95, 95
Oranges	3.00	83, 83	100, 97
	6.00	73, 80	83, 93
Alfalfa	10.00	70, 68	85, 81
	20.00	75, 77	89, 91

Adequate recoveries were obtained in all crop matrices, and at all fortification levels, for the the combined recovery of naled and DDVP, i.e., recoveries ranged from 83 to 100%. Recoveries for naled, per se, were somewhat lower, ranging from 54 to 83%.

Since the expression of tolerance (40 CFR 180.215) is written to include the combined residues of the parent, naled, and its metabolite DDVP (calculated as equivalents of naled), DEB concludes that the method RM-3G-4 with addendum is adequate for enforcement purposes in the subject crop matrices. The question of conversion of the parent compound to its metabolite DDVP (>5%) during analysis becomes moot.

The registrant should submit a revised version of method RM-3G-4 with addendum which eliminates the recommendation for a particular brand of acetonitrile, and the testing of this solvent to determine whether it converts excessive amounts of naled to DDVP. In addition, the registrant should clearly state that the calculation of residue level is to reflect the total residues of naled and its metabolite DDVP (calculated as equivalents of naled).

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