Waters Lab Highlights

An Internal Communication of Applications and Techniques

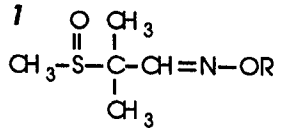
LAH 0370 6/88
AN/ES,FA,HO/
MD/PS/CU

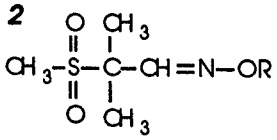
Post-Column Reaction Detection
II. Advantages of PCRD for Carbamate Analysis [1]

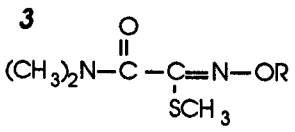
N-Methylcarbamate or N-methylcarbamoyloxime derivatives are widely used by both commercial growers and home gardeners on many fruit and vegetable crops. If carbamate pesticides have not been applied in accordance with the manufacturer's instructions, food contamination may become a problem. Additionally, runoff from fields and orchards may lead to pollution of ground water, and, potentially, drinking water sources [2].

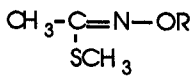
Federal and state regulations to prevent further contamination of drinking and raw source water have recently been proposed or are pending [3]. The EPA is scheduled to add carbamate pesticides to the list of National Interim Primary Drinking Water Standards (NIPDWS) in 1988. For these reasons, there is a need for reliable, sensitive, and highly specific analytical methods for carbamates and their metabolites in crop, food and water matrices.

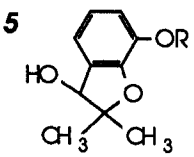
One of the problems in screening samples for the presence of carbamates and their derivatives is the variety of their chemical structures which differ widely in chromatographic retention and detection properties [see below].

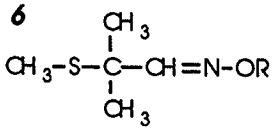

1 Aldicarb sulfoxide

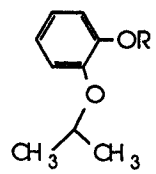

2 Aldicarb sulfone

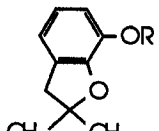

3 Oxamyl (Vydate)

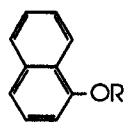

4 Methomyl (Lannate)

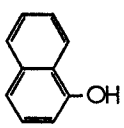

5 3-Hydroxycarbofuran

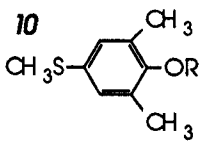

6 Aldicarb (Temik)

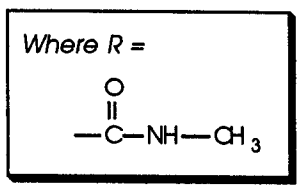

7 Propoxur (Baygon)


8 Carbofuran (Furadan)


9 Carbaryl (Sevin)


9a 1-Naphthol


10 Methiocarb (Mesurol)



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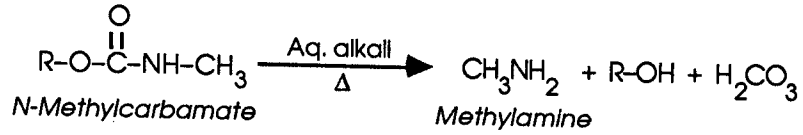
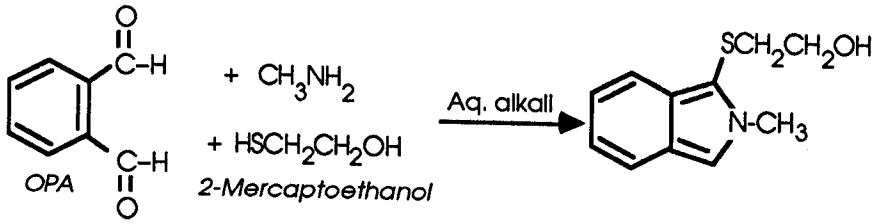
Analysis by LC is straightforward. However, when using a UV detector, the naphthalene derivative ***9*** has a detection limit more than two orders of magnitude lower than that for the aliphatic carbamoyloximes ***3*** and ***4*** [4]. This disparity can be virtually eliminated, though, by the use of the reaction detection scheme shown below, first adapted for carbamate analysis by Moye *et al.* in 1977 [5]. Following separation, the eluting carbamates are hydrolyzed to release methylamine which, in turn, is reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent isoindole derivative with optimum excitation and emission wavelengths of 339 and 454 nm, respectively [6].

Post-column Reaction Sequence for Carbamate Analysis

Step 1: Hydrolysis



Step 2: Derivatization of methylamine



This scheme has three advantages over other forms of detection: (1) it is fairly specific; (2) it is very sensitive [low ppm for crop residues; 1 ppb is typical for water samples via trace enrichment]; and (3) a single calibration curve is needed since the *identical* isoindole derivative is formed from all analytes. Variations in response are principally due to small differences in the rates of hydrolysis for each compound.

The core components, chemistry, and separation conditions of this method are embodied in E.P.A. Method 531 for drinking water [7] and the A.O.A.C. procedure for crop residue analysis [8]. Newer separation protocols have been developed by the National Pesticide Survey (EPA) [9]. In succeeding Lab Highlights we will describe methods we have found to be useful for these analyses.

* * *

References:

1. One of a recent series of Lab Highlights on PCRD; see also LAH No. 367.
2. A. Newhart, LAH, Nos. 119 and 120 (1983).
3. *Science*, **239**, 1086 (4 March, 1988).
4. T.A. Pressley and J.E. Longbottom, Method 632, *The Determination of Carbamate and Urea Pesticides in Industrial and Municipal Wastewater*, EPA (1982).
5. H.A. Moye, S.J. Scherer, and P.A. St. John, *Anal. Lett.*, **10**, 1049-1073 (1977).
6. S.S. Simons, Jr., and D.F. Johnson, *Anal. Biochem.*, **90(2)**, 705-725 (1978).
7. D.L. Foerst, Method 531, *Measurement of N-Methyl Carbamoyloximes and N-Methyl Carbamates in Drinking Water by Direct Aqueous Injection HPLC with Post Column Derivatization*, EPA (1985).
8. R.T. Krause, *J. Assoc. Off. Anal. Chem.*, **68(4)**, 726-733 (1985); ibid., 734-741 (1985).
9. Method 5, *Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Ground Water by Direct Aqueous Injection HPLC with Post Column Derivatization*, National Pesticide Survey, EPA (1987).