The Determination of HCN Residues on Greenhouse Tomatoes

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The joint action by USDA and HEW[1] in discontinuing the registration of all products specifying uses involving reasonable expectation of small residues on food or feed at harvest in the absence of a finite tolerance or exemption affects the use of pesticides on many minor crops, some of which are important to Ohio farmers. Re-registration of these pesticides for use on minor crops will require substantiating residue and toxicology data. One such area of concern in Ohio and other midwestern states is centered on the use of calcium cyanide in fumigating greenhouses for the control of whitefly on tomatoes, cucumbers, radishes, and lettuce. The Ohio greenhouse tomato crop, although of small total acreage due to the nature of the industry, is an important part of the state's agriculture and provides approximately 50 per cent of the nation's greenhouse tomato supply. Because of the need and interest expressed, the use of calcium cyanide as a fumigant for greenhouses was extended until December 31, 1969, to assemble data required for registration. The purpose of this study was to obtain residue data of calcium cyanide on greenhouse tomatoes.

Experimental Methods

Greenhouses in northeastern Ohio were treated with 0, 0.5, and 1.0 ounce of calcium cyanide per 1000 cubic feet on the evening of October 31, 1967. The calcium cyanide reacts with atmospheric moisture to liberate hydrocyanic acid gas. The greenhouses were opened the following morning, after venting according to label instructions, and samples collected immediately. Additional samples were collected on November 3 and 7, 1967. The experiment was repeated on the evening of November 24, 1967, at another greenhouse complex and samples collected the next morning and on November 27 and 30, 1967. Samples were quick frozen immediately upon collection and stored in a freezer at -20° until analyzed.

Samples were analyzed by the procedure developed for the determination of residual hydrocyanic acid in

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commodities as outlined in Volume II, Pesticide Reg. Sec. 120.130, of the Pesticide Analytical Manual (2). The sensitivity of the method was improved considerably by increasing the tomato sample size to 500 grams and filtering the distillate through a millipore filter to reduce turbidity prior to titrating the hydrocyanic acid with .01 N $AgNO_3$ against a black background. The micro-buret used was graduated to 0.02 ml. Recovery studies were conducted on tomato samples that were fortified with from 0.2 to 20 P.P.M. HCN equivalent from a potassium cyanide solution.

Results and Discussion

The recovery of HCN residues from tomatoes purchased locally and also obtained from control and treated greenhouses was very satisfactory (Table 1) except at the lower concentration of 0.2 P.P.M. which apparently was the limit of sensitivity. The background of different control samples appeared to be dependent upon the type and ripeness of the tomato. Red tomatoes purchased at a local grocery required from 0.72 to 0.92 ml of .01 N $AgNO_3$ titrant for the background (5 control samples with an average of 0.82 ml titrant) in contrast to 0.12 to 0.38 ml titrant for the green tomatoes obtained from the greenhouse (20 control samples with an average of 0.23 ml titrant). Also greater difficulties with sample foaming in the distillation flask were experienced with tomatoes that had not been frozen prior to analysis.

Residues of HCN found on greenhouse tomatoes following the fumigation treatment are recorded in Table 2. The values represent the average of triplicate analyses of each sample and are corrected for the background in untreated greenhouse tomatoes collected on the same respective day of sampling.

The residue values reported in Table 2 are all well below the limit of sensitivity of the method indicated previously in the discussion. Residues appear to be erratic and inconclusive but are reflective of the variation encountered in the analysis at this insignificant residue level. The average apparent residue in the untreated samples ranged from 0.18 to 0.29 P.P.M. whereas variation between the triplicate analyses of the same control was from zero to two times the lower value. Consequently, the residues reported in Table 2 are not significant and may only reflect variations in the results of analysis at and below the limit of sensitivity.

TABLE 1

Recovery of HCN from Tomatoes

Red tomatoes (purchased locally)						
% Recovery						
20 ppm	10 ppm	4 ppm	2 ppm	1 ppm	0.4 ppm	0.2 ppm
95.5	101.7	103.0	79.5	81.7		
93.4	97.2	105.8	87.7	96.0		
94.8		102.4				
Green tomatoes (greenhouse)						
				102.0	113.1	133.1
				91.7	102.0	71.6
				106.2	146.0	50.2
						127.0
						121.3

TABLE 2

HCN Residues in Greenhouse Tomatoes

Treatment Date	Day of Sampling	P.P.M. HCN Residue Found: 0.5 oz $Ca(CN)_2$ Treatment	P.P.M. HCN Residue Found: 1.0 oz $Ca(CN)_2$ Treatment
10/31/67	1	0.12	0.08
	3	0.09	0.12
	7	0.07	0.00
11/24/67	1	0.05	0.07
	3	0.12	0.00
	6	0.06	0.08

It is concluded that treatment of greenhouses with 0.5 and 1.0 oz. of calcium cyanide followed by the recommended practice of thoroughly airing the greenhouse after treatment will not result in HCN residues on the tomato fruit. There does not appear to be any residues of significance present on the fruit even on the first day following fumigation.

References

1. FEDERAL REGISTER, Vol. 31, No. 71, pp. 5723-24, April 13, 1966.

2. PESTICIDE ANALYTICAL MANUAL, Vol. II. Methods for Individual Pesticide Residues, compiled and edited by R.E. Duggan, H.C. Barry, L.Y. Johnson, and S. Williams.