PP# 1E1122 08/02/1974

PP# 1E1122. 2,4-D in or on potat
of amendment of 5-29-74.

Coordination Branch
and Toxicology Branch, HD

136845

In our initial review of 6-8-71
studies reflecting the proposed
of residues with and without the
to free any bound residues of 2,
requested some studies in which
dichlorophenol (2,4-DCP) was an
the 1968 North Dakota study, als
submitted previously, our questions regarding this deficiency
have been resolved (see G.J. Beusch review of 2-25-72).

In this amendment a report by Dr. D. Bristol, North Dakota State University was submitted which includes a study of the conditions for hydrolysis of bound residues in potatoes plus residue data for potatoes treated according to the recommended use and analyzed both with and without preliminary hydrolysis. Optimum conditions for hydrolysis of macerated tuber samples were obtained with a 1 hour refluxing (96°C) in 2N H_2SO_4. (Alkaline hydrolysis either in water or methanol was accompanied by excessive foaming of macerated potato tissue and resulted in the formation of intractable gels; nosuch difficulty was encountered with acid hydrolysis). Recoveries of 2,4-D from potato tissues fortified at the 0.2 ppm level showed no significant trend when the length of reflux period (in 2N H_2SO_4) was varied from 1-16 hours. Some decrease in levels of 2,4-DCP was noted with the longer reflux period.

The method finally adopted for total residue analysis (TRA) involves maceration of potato tissues in basic solution, followed by acidification and refluxing for 1 hour in 2N H_2SO_4. The mixture is then made alkaline, filtered, and the acidified filtrate extracted with benzene. Residues in the benzene extract are partitioned into alkali, acidified and extracted with ether. Separation of the phenoxy acid and phenol is achieved by passing the ether solution through an acidic alumina column. The acid (2,4-D) is retained on the column while the phenol passes through. The effluent (containing the 2,4-DCP) is concentrated and cleaned up by extraction with alkali followed by acidification and extraction with benzene. The benzene extract is analyzed directly by GC (using conductivity detection in the halogen mode). The 2,4-D is eluted from the column with sodium bicarbonate solution, the eluate acidified and extracted with ether. The ether extract is then esterified with diazomethane or diazoethane and the ester analyzed by GC.

Recoveries of 2,4-D (0.02-0.2 ppm fortification levels) were from 84-90%; for 2,4-DCP (0.002-0.02 ppm) values were 79-93%. Controls were reported as <0.02 ppm for 2,4-D and <0.002 ppm for 2,4-DCP. We consider this method to be adequately validated and suitable for enforcement purposes. A similar procedure in PAM (Vol. I, Section 222.1) is also available for determining total residues of 2,4-D and the phenol. This procedure when modified to include an acid reflux step, will determine both free and bound residues.

Free residues of 2,4-D and 2,4-DCP were determined by the former procedure omitting the reflux (hydrolysis) steps.

Residue studies were conducted in 1972 and 1973 which reflected the proposed conditions of use with application rates of 1 and 2X. Total free and bound residues were determined for both studies; free (unbound) residues were determined for comparison in the 1972 studies.

Total residues of 2,4-D ranged from 0.07-0.15 ppm in all cases; total residues of 2,4-DCP were present in only trace amounts, 0.01 ppm or less. Free (unbound) residues of 2,4-D ranged from 0.05-0.13 ppm and averaged about 10-20% less than the corresponding values for total residues. Free residues of 2,4-DCP were not detected (<0.005 ppm) in the potato samples.

In this amendment the proposed tolerance for 2,4-D in potatoes has been raised from 0.1 to 0.2 ppm. Based on the above studies (as well as those submitted previously) we conclude that [illegible] total residues of 2,4-D (and 2,4-DCP) will not exceed this level from the proposed use on potatoes. We believe that the tolerance proposal in terms of 2,4-D only is appropriate since residues of 2,4-DCP are present in trace amounts only and TB (K. Engler memofof 7-17-74) has already concluded that these levels are of no toxicological concern.

We reiterate our previous conclusion that the level of residues from this use is such that the feeding of treated potatoes will not change the present Category 2 situation of Section 180.6(a) with respect to meat and milk. Residues resulting in meat and milk from the present use on potatoes would be insignificant in relation to both the established tolerances on feed items and to the proposals in PP# 8F0670 (currently under consideration), in which tolerances of 300 ppm are sought on rangeland and pasture grasses. Appropriate meat and milk tolerances (as well as poultry and egg tolerances, if needed) will also be established when deficiencies in this petition (PP# 8F0670) are resolved.

Recommendations

Toxicological considerations permitting, we recommend that the proposed tolerance of 0.2 ppm for residues of 2,4-D in or on potatoes be established. When this tolerance is established, the interim tolerance for 2,4-D on potatoes should be deleted from the Regulations.

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