MEMORANDUM

SUBJECT:  Reregistration of Pyrethrins: Analytical Method Issues; Chemical No. 69001; Case No. 2580; Branch No. 9756; DP Barcode No. D177182

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The Pyrethrum Joint Venture (PJV) has submitted a justification for quantitation of pyrethrum residues in crops based on analysis of pyrethrins I esters only. The PJV claims that thermal degradation (in the GC column and injection port) of the pyrethrins II esters precludes reliable quantitation.

In support of their argument the PJV has submitted a document which includes copies of two literature references, attempts by two contract labs at chromatographing the pyrethrins under various conditions, and results of photostability testing.

Holmstead and Soderlund [Pyrethrum Post 14 (3) 79] were able to separate all six esters with minimal degradation using GLC-MS under chemical ionization conditions. This method would not be applicable to residue analysis because of sensitivity problems. Wiebolt et al (Journal of High Resolution Chromatography, Vol 12, 1989 pp. 106-111) observed thermal degradation of pyrethrin 1 and pyrethrin 2 esters under capillary GC conditions, but were able to separate all six esters and reliably quantitate them using capillary super-critical fluid chromatography (SFC) with infrared detection (IR).
When two contract labs attempted to duplicate the GC conditions of Wiebolt, similar thermal degradation problems were obtained. Pyrethrin I ester seems to be less subject to degradation than pyrethrin 2. The PJV states that levels of pyrethrins I esters and pyrethrins II esters are approximately equal in pyrethrum extract. Photostability testing was conducted to determine if the pyrethrins I and II esters are equally photolabile. Degradation rates were not significantly different.

CBRS Comment

From the information presented there is more difficulty chromatographing the pyrethrins II esters, especially pyrethrin 2. If pyrethrins residues are present in/on treated commodities the proportional amount of pyrethrins I esters (as compared to pyrethrins II) should be sufficient for quantitation. Although all six esters may be reliably quantitated using SFC/IR, this equipment is not routinely available in enforcement laboratories, so its use would not be appropriate in enforcement methods. Since these chemicals are unique in being naturally-occurring and rapidly degraded in the environment, CBRS has no objection at this time to the PJV quantitating only the pyrethrins I esters (specifically pyrethrin 1, jasmolin 1, and cinerin 1) in the magnitude of the residue and storage stability studies required for the reregistration of pyrethrins.

Although CBRS has no objection at this time, conditions may exist at a later date which would require generation of pyrethrins II data. It should be noted that the metabolism studies have not been completed. Review of these studies may result in a revision of our position depending upon which compounds are considered to be of concern.

cc: CLOlinger (CBRS), Circulate, List B File, RF, SF, C. Furlow (PIB/FOD)
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