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SUBJECT: PP# 3F1370. Method tryout for the chlorpyrifos metabolite 3,5,6-Trichloro-2-pyridinol (TCP) in bananas. DATE: MAR 7 1975

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We have completed a tryout of the Dow Chemical Company method entitled: "Determination of Residues of 3,5,6-Trichloro-2-pyridinol in Bananas by Gas Chromatography" (Dow ACR 72.13). Whole bananas fortified with TCP at the 0.05 and 0.10 ppm levels and crop blanks were run in duplicate.

Our results indicate that the method is satisfactory for determining residues of TCP in bananas at the aforementioned fortification levels. Apparent residues of TCP in the crop blanks were less than 0.005 ppm. Recoveries of TCP from samples fortified at levels of 0.05 and 0.10 ppm were 88-94% and 91-98%, respectively.

Details of the Method Trial

The analytical procedure involves extracting the sample with methanol and passing an aliquot of the filtered extract through an acid alumina column. The TCP is eluted from the column with aqueous hydrochloric acid solution, partitioned into benzene, and extracted from the benzene into aqueous sodium bicarbonate solution. After the alkaline solution is acidified, the TCP is partitioned into benzene and treated with N,O-bis(trimethylsilyl) acetamide (BSA) to form a trimethylsilyl derivative which is determined by election capture gas chromatography.

A Barber-Colman Model 5000 Gas Chromatograph equipped with a tritium ionization source election capture detector was used for the tryout. The operating parameters (these differ somewhat from those given in Dow ACR 72.13 for use with a ^{90}Sr election capture detector) were as follows:

Column: 6' x 4 mm id glass "U" tube, packed with 5% DC-200 silicone oil on 80/100 mesh Gas Chrom Q.

Temperatures: Column, 120°C; injector, 210°C; detector, 205°C.

Carrier gas: Nitrogen @ 100 ml/min.

Electrometer sensitivity: 3×10^{-10} AFS into a 5 mv recorder.

Detector voltage: 10 volts.

At these conditions, TMS-TCP (the trimethyl silyl derivative of 3,5,6-trichloro-2-pyridinol) had a retention time of approximately 6 minutes and the response for 75 picograms of TCP (after conversion to TMS-TCP) was approximately 30% FSD.

Standard solutions of TMS-TCP were prepared by treating known amounts of TCP with BSA as described in Dow ACR 72.13. These standards were prepared in duplicate to give an indication of the reproducibility of the derivative formation. The heights of the GLC peaks for TMS-TCP in duplicate runs were practically identical, showing that the derivative formation was reproducible. (Since an analytical standard of pure TMS-TCP was not available for the try-out, the efficiency of the derivatization procedure could not be determined.)

The chromatograms of reagent blanks carried through the entire procedure showed no peaks at the retention time of TMS-TCP. Since several vials of BSA were used in the tryout, each was tested for possible interferences before use in the analysis of crop samples. No interferences were found in the BSA.

No difficulties were encountered in the analysis of whole bananas. The method (Dow ACR 72.13) was followed as written, except that we did not use a centrifuge in the partitioning steps since almost perfect separation between the aqueous and organic phases was obtained without centrifugation. The results of the method trial were as follows:

3,5,6-trichloro-2-pyridinol (TCP) in Whole Bananas

Sample No.	TCP Added (ppm)	TCP Found (ppm)	Recovery (%)
1	none	<0.005	---
2	none	<0.005	---
3	0.05	0.044	88
4	0.05	0.047	94
5	0.10	0.091	91
6	0.10	0.098	98

cc: PP# 3F1370
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