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MEPIQUAT CHLORIDE
(Chemical Code 109101)
(CBRS No. 10229; DP Barcode D180700)

TASK 2B

Reregistration Review
Residue Chemistry

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PHASE 5 - REREGISTRATION REVIEW RESIDUE CHEMISTRY

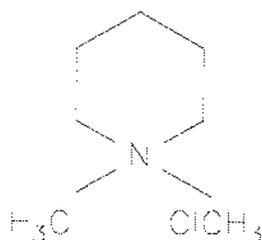
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BACKGROUND

The Mepiquat Chloride Phase 4 review, dated 10/31/90, required a new plant metabolism study. In response, BASF Corporation (1992; MRID 42330804) submitted data on metabolism of [¹⁴C]mepiquat chloride in cotton. These data are reviewed in this report for adequacy in fulfilling outstanding residue chemistry data requirement. The Conclusions and Recommendations stated herein pertain only to the qualitative nature of the residue in plants.

The Phase 4 Review required a new cotton metabolism study and additional data from existing animal metabolism studies. Established tolerances for residues in or on cottonseed and cotton forage and in animal commodities are expressed in terms of the parent compound N,N-dimethylpiperidinium chloride per se (40 CFR §180.384). Adequate enforcement methodology is available in PAM, Vol. II, Method I.

There are no established or proposed Codex MRLs for mepiquat chloride. Therefore, no compatibility questions exist with respect to U.S. tolerances and Codex.



Mepiquat Chloride

CONCLUSIONS

1. The submitted cotton plant metabolism study is adequate. The parent compound, mepiquat chloride, is the residue to be regulated, accounting for >90% of the total radioactive residue in cotton forage and cottonseed. Since the free parent is the residue of concern and since the PAM II method utilizes an extraction procedure similar to that used in this metabolism study, the radiovalidation study on cottonseed is waived.

DETAILED CONSIDERATIONS

Qualitative Nature of the Residue in Plants

BASF Corporation (1992; MRID 42330804) submitted data on the metabolism of [^{14}C]mepiquat chloride in cotton. [2-, 6- ^{14}C]Mepiquat chloride (specific activity 40.813 ·Ci/mg, 90,605 dpm/g; radiochemical purity >99%) with AG 98 surfactant was sprayed on cotton plants in the first bloom stage (25-27 inches) at a rate equivalent to 0.14 lb ai/A (3x the maximum registered single application rate). Samples were taken from the plants 15 and 51 days after treatment and plants were harvested at 67 days. Samples were stored at -15 °C until analysis.

Total Radioactive Residues (TRR)

Prior to radio-analysis, the 15-day plants were separated into roots, stems, leaves/petioles, and bolls; the 51-day plants were separated into stems, leaves/petioles, and bolls; and the 67-day plants were kept intact after removal of cotton/seeds. Each of these fractions was radioassayed for total ^{14}C -residues by combustion and liquid scintillation spectrometry (LSS). The submission reported dpm radioactivity in each sample and provided sample weights. From these data and the specific activity in the [^{14}C]mepiquat chloride applied, TRRs were calculated for forage (stems plus leaves/petioles) and seed samples. These TRRs are summarized in Table 1.

The TRR values used in subsequent tables are based on the total of extracted and unextracted residues in the samples chosen for analysis and not the TRR values obtained by combustion. In the case of 15-day forage, the sample used for extraction and analysis consisted of equal weights of the stem and leaf/petiole parts. This TRR value was higher than that obtained from combustion, because the proportion of the leaves/petioles (tissues with the highest ^{14}C - residues) was 50% in the extracted samples but only about 20% in the combusted samples.

Table 1. Total radioactive residues (TRR) in cotton forage and cottonseed treated with [^{14}C]mepiquat chloride at 3x.

Matrix	TRR combustion ^a	TRR extraction ^b
Plant (15-day)	0.224	0.419 ^c
Plant (51-day)	0.469	--

Forage (67-day)	0.781	0.870
Seed (67-day)	0.936	0.948, 0.961

^aCalculated by reviewer using values submitted by the registrant for total dpm in sample, sample weight, and specific radioactivity of the test substance. ^bTRR of samples used for residue analysis, based on the sum of solvent-extracted and insoluble residues. ^cWhole plant sample used for analysis was reconstituted from separated plant parts, using equal weights of leaf/petiole and stem components.

Extraction of Residues

Radioactive residues from forage (combined equal weights of stem and leaf/petiole samples) from the 15-day plants and from the whole (cotton/seed removed) 67-day plants were extracted with 0.1 N methanolic HCl (MeOH/HCl). The extract was loaded onto an aromatic sulfonic acid cation exchange column from which the residues were eluted with 5 N HCl. The eluant was evaporated to dryness and the residues were redissolved in water and adjusted to pH 13 with NaOH. The ¹⁴C-residues were partitioned into dichloromethane containing dipicrylamine (DCM/DPA) then into 2 N HCl. The HCl was evaporated and the residues were dissolved in MeOH and analyzed by TLC using two solvent systems. The results are summarized in Table 2.

Two cottonseed samples were extracted with hexane to remove oils then residues were extracted with MeOH/HCl and subjected to cation exchange column and solvent partition cleanup and TLC analysis as described for forage. The results shown in Table 3 represent the averages from the analysis of the two samples. The insoluble fractions from the two samples were refluxed for 4 hours in 1% NaCl, centrifuged, and the resulting NaCl supernatants were subjected to two additional analyses. In the first sample, a "starch" fraction was precipitated by the addition of methanol and "protein" was precipitated by the addition of acetonitrile. The remaining soluble residues were cleaned up via column and solvent partitioning and analyzed by TLC as described previously for forage. The residues in the 1% NaCl from the second sample were adjusted to pH 13, partitioned into DCM/DPA then into HCl. The pH adjustment and partitioning steps were repeated, and the HCl was removed by evaporation. Residues were redissolved in MeOH and analyzed by TLC. The results of analyses of the initial insoluble fractions from cottonseed are summarized in Tables 4 and 5.

Table 2. Distribution of ¹⁴C-residues in fractions from 15- and 67- day cotton forage, including results of TLC analysis for [¹⁴C]mepiquat chloride.

Fraction	15-day Plant	67-day Plant
	% TRR (ppm)	% TRR (ppm)
MeOH/HCl	97.0 (0.406) ^a	95.4 (0.830)
Cation exchange column eluate	106.8 (0.447)	105.2 (0.915)
Solvent partition	92.1 (0.385)	91.2 (0.793)
TLC: ^b		
mepiquat chloride	90 (0.337)	91.2 (0.793)
other	2.1 (0.009)	0 (0)

Insoluble residues	3.0 (0.013)	4.6 (0.04)
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^aExpressed as mepiquat chloride equivalents. ^bAverage of results using two solvent systems.

Table 3. Distribution of ¹⁴C-residues from cottonseed^a.

Fraction	% TRR ^b	ppm
Hexane	1.2	0.01
MeOH/HCl	86.1	0.822
cation exchange column	84.6	0.806
solvent partition	92.2	0.868
TLC:		
Mepiquat chloride	90.6	0.863
other	0.6	0.006
Insoluble residues	12.8	0.122
1% NaCl	7.8	0.075
residual solids	5.0	0.048

^aResults are the averages of two samples. ^bTRR = total hexane extractable, MeOH/HCl extractable, and insoluble; average for the two samples was 0.954 ppm.

Table 4. Analysis of cottonseed insoluble fraction: procedure 1.

Fraction	%TRR	ppm
Insoluble fraction 1	12.5	0.119
1% NaCl	7.1	0.068
starch	0.6	0.006
protein	0	0
supernatant	6.7	0.064
cleanup	3.6	0.035
Mepiquat chloride	3.3	0.032
other	0.3	0.003
Residual Solids	5.1	0.049

Table 5. Analysis of cottonseed insoluble fraction: procedure 2.

Fraction	% TRR	ppm
Insoluble fraction 2	13.0	0.125
1% NaCl	8.5	0.082
1 st partition	9.4	0.091
cleanup	4.8	0.046
TLC:		

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Mepiquat chloride	4.8	0.046
<u>Residual Solids</u>	<u>4.8</u>	<u>0.046</u>

Characterization of Residues

TLC analyses were conducted on silica gel plates using two solvent systems. Samples were co-chromatographed with an authentic [^{14}C]mepiquat chloride standard. Radioactivity on TLC plates was quantitated by direct integration with a radioanalytic imaging system.

The TLC results are included in Tables 2 through 5. The parent mepiquat chloride was the only ^{14}C -residue detected in any of the extracts, accounting for 90 and 91.2% of the TRR in 15- and 67-day forage, respectively, and 96.6 and 92.6% of the TRR in two cottonseed samples.

This study is adequate. No additional data on cotton metabolism of mepiquat chloride are required. The parent compound, mepiquat chloride, is the residue to be regulated in cotton. Since the free parent is the residue of concern and since the PAM II method utilizes an extraction procedure similar to that used in this metabolism study, the radiovalidation study on cottonseed is waived.

References

Citations for the MRID documents referenced in this review are presented below. Submissions reviewed in this document are indicated by shaded type.

- 42330804 Goetz, A. (1992) Metabolism of ^{14}C -BAS 083 in Cotton (*Gossypium hirsutum*): BASF Report No. M9203. Unpublished study prepared by BASF Corp. p. 90.

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