List A Reg. 9

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUN 11 1996

MEMORANDUM

OFFICE OF
PREVENTION, PESTICIDES, AND
TOXIC SUBSTANCES

SUBJECT: **2,4-D.** (030066) Enforcement Analytical Method for IPE in Citrus Commodities. GDLN 171-4(c).
DP Barcode: D222627; CBRS No. 16878; MRID No.: 438937-01; Rereg. Case No. 0073.

FROM: David J. Miller, HSO, U.S. Public Health Service
Chemistry Pilot Review Team
Chemistry Branch II--Reregistration Support
Health Effects Division (7509C)

THRU: Edward Zager, Chief
Chemistry Branch II--Reregistration Support
Health Effects Division (7509C)

RB Perfetti for

TO: Paula Deschamp, Section Head
Reregistration Section
Risk Characterization and Analysis Branch
Health Effects Division (7509C)

CBRS has been requested to review an analytical method submitted by the California Citrus Quality Council for the determination of 2,4-D in/on citrus fruits and their processed commodities.

The 2,4-D Guidance Document, dated 9/88, required that representative samples from plant and animal metabolism studies be analyzed using suitable tolerance enforcement methods. This requirement was reiterated in conjunction with Agency reviews of 2,4-D metabolism studies on wheat (CBRS Nos. 10466, 11197, and 11219, DP Barcodes D181885, D186732, and D186927, 4/6/93, R. Perfetti) and lemons (CBRS Nos. 14067, DP Barcodes D205343, 1/6/95, R. Perfetti).

The nature of the residue in plants is adequately understood. Acceptable wheat, lemon, and potato metabolism studies have been submitted. The nature of the residue in animals is adequately understood based upon acceptable ruminant and poultry metabolism studies. The HED Metabolism Committee (6/16/93) has concluded that the residue of concern is 2,4-D *per se* in wheat and similar plants, with a subsequent CBRS memorandum concluding that the metabolism in lemons is similar to that in wheat.

Tolerances for residues of 2,4-D in/on plant, processed food/feed, and fish commodities are expressed in terms of 2,4-D *per se* [40 CFR §180.142 (a through f, i, j, and k), 40 CFR §185.1450 (a), and 40 CFR §186.1450]. Tolerances in animal commodities are currently expressed in terms of residues of 2,4-D and/or its metabolite 2,4-dichlorophenol [40 CFR §180.142 (h)].

Three GC methods with microcoulometric detection (MCD) and one GC/ECD method are listed in the PAM, Vol. II as Methods A, B, C, and D.

The Codex MRLs are expressed in terms of residues of 2,4-D *per se*. The Codex MRL and the U.S. tolerance expression are compatible for plant commodities only, pending incorporation of HED Metabolism Committee recommendations into the tolerance expression for animal commodities. Issues regarding harmonization of the U.S. tolerances with the Codex MRLs will be addressed when the reregistration eligibility of 2,4-D is determined.

CONCLUSIONS/RECOMMENDATIONS

1. The GC/MSD method is adequate for determining residues of 2,4-D in/on citrus RACs and processed commodities. The validated limit of quantitation (LOQ) for this method is ca. 0.02 ppm.

2. The registrant has submitted five separate methods for the various raw and processed commodities of citrus. As all of the methods involve the same basic extraction procedures, reagents, and analytical instrumentation, the methods should be combined into a single method which describes the specific differences for each matrix (e.g., different extraction reagent molarities, etc.).

3. The method should remove from the method write-up any reference to correcting (or adjusting) the sample 2,4-D levels for the concentration of 2,4-D found in control samples. This adjustment in inappropriate.

4. The registrant should clarify the method used to develop the standard curve, since it is unclear if the curve is developed from matrix-spike samples. The registrant is reminded that an analytical enforcement method must not require that blank matrix samples be available. If blank matrix samples are required, the method should be rewritten to delete their use.

5. The registrant indicated that the LOQ for citrus racs, lemon juice, and lemon wet pulp was 0.05 ppm, that the LOQ for lemon dry pulp and molasses was 0.2 ppm, and that the LOQ for lemon oil was 0.5 ppm. However, CBRS inspection of the chromatograms and recovery values calculated above suggest that actual LOQs are at least a factor of 2 lower than these registrant-estimated values since adequate recoveries at 50% of the registrant's

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LOQ was demonstrated. The registrant should indicate a more appropriate method LOQ (which will at a later time be validated and confirmed by EPA Beltsville). The registrant should also refrain from referring to the LOQ as the method "sensitivity" and instead report it as LOQ or LOD as appropriate.

6. Radiolabel validation was performed to evaluate the extraction efficiency of the method. Lemon peel stored for a 20 week post-treatment interval from a previous metabolism study was combusted, with the evolved $^{14}CO_2$ counted by LSC. From these results, the extraction of the GC/MSD method was 98%. CBRS concludes that these data indicate that California Citrus Quality Council's proposed enforcement method is capable of adequately recovering residues of 2,4-D from treated lemon peel and, by extension, from all raw and processed citrus commodities, provided that a revised method incorporating Conclusions #2 through 5 is submitted. When this new method write-up is submitted, CBRS will forward the method to the Agency's Analytical Chemistry Laboratory (Beltsville, MD) for tolerance method validation.

DETAILED CONSIDERATIONS:

Hazleton Wisconsin (HWI) developed several matrix-specific methods to determine 2,4-D residues in/on raw oranges, lemons, and grapefruits and the following processed lemon products: juice, wet pulp, dry pulp, molasses, and oil.

Several different methods were developed and validated for the determination of 2,4-D in the rac and processed commodities of interest. The matrix-specific methods are briefly summarized below:

Oranges and Grapefruit: 2,4-D is extracted from a ten gram rac sample with 0.2M NaOH for 1 hour at 100 C. An aliquot of the extraction solvent is acidified and extracted a second time with ethyl ether, with the ether extract derivatized to the 2,4-D methyl ester (2,4-D ME) with a boron trifluoride/methanol solution. Water is added, the sample is brought to volume in hexane, and analyzed by GC/MSD.

Lemons, Lemon Juice, and Lemon Wet Pulp: The method is the same as that described above for oranges and grapefruit, except that 0.7 M NaOH is used for extraction.

Lemon Dry Pulp: 2,4-D is extracted from a 2 gram sample of pulp by overnight extraction with 0.7 M NaOH followed by heating for 1 hour and 100 C. An aliquot of the extraction solution is acidified and extracted with ethyl ether. The ethyl ether extract is then derivatized to 2,4-D ME as described above. Finally, water is added, the sample is brought up in hexane, and is analyzed by GC/MSD.

Lemon Molasses: 2,4-D is extracted from a 5 gram sample of molassess with 0.2 M NaOH for 1 hour at 100 C. An aliquot of the extraction solution is acidified and extracted with ethyl ether. The ether extract is derivatized to the 2,4-D ME as detailed above, water is added, the sample brought up in hexane, and analysis is performed on

a GC/MSD.

Lemon Oil: 2,4-D is extracted from a 1 g sample of lemon oil with 0.2 M NaOH for 2 hours at 100 C. The extraction solution is acidified and extracted with ethyl ether, with the ethyl ether extract derivatized to 2,4-D ME as before. After addition of water, the sample is brought up in hexane and analyzed by GC/MSD.

The recovery calculations are presented in Tables 1 and 2 for raw and processed commodities, respectively. As can be seen, fortification recoveries were acceptable in all raw and processed commodities. CBRS makes the following points with respect to the registrant's proposed analytical enforcement method.

- the registrant has submitted five separate methods for the various raw and processed commodities of citrus. As all of the methods involve the same basic extraction procedures, reagents, and analytical instrumentation, the methods should be combined into a single method which describes the specific differences for each matrix (e.g., different extraction reagent molarities, etc.).

- the registrant should remove from the method write-up any reference to correcting (or adjusting) the sample 2,4-D levels for the concentration of 2,4-D found in control samples. This adjustment is inappropriate.

- the registrant should clarify the method used to develop the standard curve, since it is unclear if the curve is developed from matrix-spike samples. The registrant is reminded that an analytical enforcement method must not require that blank matrix samples be available. If blank matrix samples are required, the method should be rewritten to delete their use.

- while the registrant indicated that the LOQ for citrus racs, lemon juice, and lemon wet pulp was 0.05 ppm, that the LOQ for lemon dry pulp and molasses was 0.2 ppm, and that the LOQ for lemon oil was 0.5 ppm, CBRS inspection of the chromatograms and recovery values calculated above suggest that actual LOQs are at least a factor of 2 lower than these registrant-estimated values since adequate recoveries at 50% of the registrant's LOQ was demonstrated. The registrant should indicate a more appropriate method LOQ (which will at a later time be validated and confirmed by EPA Beltsville). The registrant should also refrain from refering to the LOQ as the method "sensitivity" and instead report it as LOQ or LOD, as appropriate.

Radiolabeled Method Validation

Radiolabel validation was performed to evaluate the extraction efficiency of the method (after the radiovalidation, the method was modified to use a stronger extraction solvent and precipitation solution). Lemon peel from a 20 week post-treatment interval sampled from a previous metabolism study (MRID 43290501) was brought to room temperature and combusted, with the evolved $^{14}CO_2$ counted by LSC: the radioactivity concentration of the lemon peel was

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68949 dpm/g. Since the specific activity of the applied 2,4-IPE was 11849 dpm/ug, the TRR in the lemon peel can be calculated as 5.8 ppm (i.e., 68949 dpm/g divided by 11849 dpm/ug). Since the previous metabolism study identified 64.6% of the TRR in 20 week lemon peel sample as 2,4-D (or 2,4-D IPE), the present radiovalidation showed 3.7 ppm 2,4-D (i.e., 64.6% x 5.8 ppm). Since the average residue found by GC/MSD in lemon peel was 3.61 ppm (as 2,4-D), the percent recovery of the GC/MSD can be calculated as 98%. (NOTE: This calculation differs somewhat from that provided in the registrant's submission in that the registrant incorrectly calculated the concentration of 2,4-D (and not TRR) as 5.8 ppm).

The registrant also performed a material balance of the lemon peel sample in which the majority (ca. 80%) of the recovered radioactivity was shown to concentrate in the hexane fraction. Since it is the hexane fraction that is analyzed by GC/MSD, this provides further support of the adequacy of the proposed enforcement method.

CBRS concludes that these data indicate that California Citrus Quality Council's proposed enforcement method is capable of adequately recovering residues of 2,4-D from treated lemon peel and, by extension, from all raw and processed citrus commodities.

RDI: Pilot Team:6/6/96;RPerfetti:6/7/96.
cc: RF, SF, List A Rereg. F., Circ., J. Coombs (SRRD), DJM.

Table 1. Recovery Values for the Fortification of 2,4-D in Raw Oranges, Grapefruit, and Lemon.

Commodity	Fortification Level (ppm)	Concentration Found (ppm)	Percent Recovery
Oranges[a]	Control	0.00730	NA
	0.025[b]	0.0346	138
	0.025[b]	0.0322	129
	0.0500	0.0654	131
	0.0500	0.0627	125
	0.100	0.111	111
	0.100	0.115	115
	0.250	0.278	111
	0.250	0.274	110
Grapefruit	Control	ND	NA
	0.0100[b]	0.0121	121
	0.0100[b]	0.0123	123
	0.0250[b]	0.0249	100
	0.0250[b]	0.0254	102
	0.0500	0.0534	107
	0.0500	0.0520	104
	0.100	0.0987	99
	0.100	0.100	100
	0.200	0.191	96
	0.200	0.195	98
Lemon	Control	ND	NA
	0.0250[b]	0.0247	99
	0.0250[b]	0.0263	105
	0.0500	0.0540	108
	0.0500	0.0533	107
	0.100	0.106	106
	0.100	0.103	103
	0.250	0.241	96
	0.250	0.248	99

[a] For oranges, the registrant calculated an "adjusted" ppm value which corrected for the 0.00739 ppm 2,4-D detected in the control sample. CBRS does not believe that this correction is appropriate and has instead calculated percent recoveries without the adjustment direction from the ppm found value.
[b] The registrant states that these samples were run to either evaluate the sensitivity (i.e., LOQ/LOD) of the instrument or to evaluate analysis at 50% of the LOQ and that these results were not included in their calculation of the mean recoveries or standard deviations.

Table 2. Recovery Values for the Fortification of 2,4-D in Lemon Juice, Wet Pulp, Dry Pulp, Molasses, and Oil.

Commodity	Fortification Level (ppm)	Concentration Found (ppm)	Percent Recovery
Lemon Juice	Control	ND	NA
	0.0250[a]	0.0270	108
	0.0250[a]	0.0231	92
	0.0500	0.0529	106
	0.0500	0.0524	105
	0.100	0.0944	94
	0.100	0.101	101
	0.250	0.238	95
	0.250	0.222	89
Lemon Wet Pulp	Control	ND	NA
	0.0250[a]	0.0221	88
	0.0250[a]	0.0256	102
	0.0500	0.0545	109
	0.0500	0.0533	107
	0.100	0.0973	97
	0.100	0.0924	92
	0.250	0.237	95
	0.250	0.216	86
Lemon Dry Pulp	Control	ND	NA
	0.100[a]	0.0889	89
	0.100[a]	0.0869	87
	0.200	0.173	87
	0.200	0.165	83
	1.00	0.746	75
	1.00	0.711	71
	2.00	1.43	72
	2.00	1.35	68
	2.00	2.03	102
	2.00	1.88	94

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Lemon Molasses	Control	0.0112	NA
	0.100[a]	0.109	109
	0.100[a]	0.115	115
	0.200	0.213	107
	0.200	0.199	100
	1.00	0.754	75
	1.00	0.783	78
	2.00	1.91	96
	2.00	1.97	99
Lemon Oil	Control	ND	NA
	0.500	0.429	86
	0.500	0.454	91
	1.00	0.864	86
	1.00	0.937	94
	2.00	1.58	79
	2.00	1.78	89
	5.00	4.32	86
	5.00	4.21	84

[a] The registrant states that these samples were run to evaluate the analyses at 50% of the LOQ and that the results were not included in their calculation of the mean recovery and its associated standard deviation.

Sub; File

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Lemons, Lemon Juice, and Lemon Wet Pulp: The method is the same as that described above for oranges and grapefruit, except that 0.7 M NaOH is used for extraction.

Lemon Dry Pulp: 2,4-D is extracted from a 2 gram sample of pulp by overnight extraction with 0.7 M NaOH followed by heating for 1 hour and 100 C. An aliquot of the extraction solution is acidified and extracted with ethyl ether. The ethyl ether extract is then derivatized to 2,4 D ME as described above. Finally, water is added, the sample is brought up in hexane, and is analyzed by GC/MSD.

Lemon Molasses: 2,4-D is extracted from a 5 gram sample of molassess with 0.2 M NaOH for 1 hour at 100 C. An aliquot of the extraction solution is acidified and extracted with ethyl ether. The ether extract is derivatized to the 2,4-D ME as detailed above, water is added, the sample brought up in hexane, and analysis is performed on

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a GC/MSD.

Lemon Oil: 2,4-D is extracted from a 1 g sample of lemon oil with 0.2 M NaOH for 2 hours at 100 C. The extraction solution is acidified and extracted with ethyl ether, with the ethyl ether extract derivatized to 2,4-D ME as before. After addition of water, the sample is brought up in hexane and analyzed by GC/MSD.

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	0.100	0.111	111
	0.100	0.115	115
	0.250	0.278	111
	0.250	0.274	110
Grapefruit	Control	ND	NA
	0.0100[b]	0.0121	121
	0.0100[b]	0.0123	123
	0.0250[b]	0.0249	100
	0.0250[b]	0.0254	102
	0.0500	0.0534	107
	0.0500	0.0520	104
	0.100	0.0987	99
	0.100	0.100	100
	0.200	0.191	96
	0.200	0.195	98
Lemon	Control	ND	NA
	0.0250[b]	0.0247	99
	0.0250[b]	0.0263	105
	0.0500	0.0540	108
	0.0500	0.0533	107
	0.100	0.106	106
	0.100	0.103	103
	0.250	0.241	96
	0.250	0.248	99

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[a] For oranges, the registrant calculated an "adjusted" ppm value which corrected for the 0.00739 ppm 2,4-D detected in the control sample. CBRS does not believe that this correction is appropriate and has instead calculated percent recoveries without the adjustment direction from the ppm found value.
[b] The registrant states that these samples were run to either evaluate the sensitivity (i.e., LOQ/LOD) of the instrument or to evaluate analysis at 50% of the LOQ and that these results were not included in their calculation of the mean recoveries or standard deviations.

Table 2. Recovery Values for the Fortification of 2,4-D in Lemon Juice, Wet Pulp, Dry Pulp, Molasses, and Oil.

Commodity	Fortification Level (ppm)	Concentration Found (ppm)	Percent Recovery
Lemon Juice	Control	ND	NA
	0.0250[a]	0.0270	108
	0.0250[a]	0.0231	92
	0.0500	0.0529	106
	0.0500	0.0524	105
	0.100	0.0944	94
	0.100	0.101	101
	0.250	0.238	95
	0.250	0.222	89
Lemon Wet Pulp	Control	ND	NA
	0.0250[a]	0.0221	88
	0.0250[a]	0.0256	102
	0.0500	0.0545	109
	0.0500	0.0533	107
	0.100	0.0973	97
	0.100	0.0924	92
	0.250	0.237	95
	0.250	0.216	86
Lemon Dry Pulp	Control	ND	NA
	0.100[a]	0.0889	89
	0.100[a]	0.0869	87
	0.200	0.173	87
	0.200	0.165	83
	1.00	0.746	75
	1.00	0.711	71
	2.00	1.43	72
	2.00	1.35	68
	2.00	2.03	102
	2.00	1.88	94

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Lemon Molasses	Control	0.0112	NA
	0.100[a]	0.109	109
	0.100[a]	0.115	115
	0.200	0.213	107
	0.200	0.199	100
	1.00	0.754	75
	1.00	0.783	78
	2.00	1.91	96
	2.00	1.97	99
Lemon Oil	Control	ND	NA
	0.500	0.429	86
	0.500	0.454	91
	1.00	0.864	86
	1.00	0.937	94
	2.00	1.58	79
	2.00	1.78	89
	5.00	4.32	86
	5.00	4.21	84

[a] The registrant states that these samples were run to evaluate the analyses at 50% of the LOQ and that the results were not included in their calculation of the mean recovery and its associated standard deviation.

13544

R102533

Chemical:	**2,4-D, isopropyl ester**
PC Code:	**030066**
HED File Code	**11200 Subject Files Chemistry**
Memo Date:	**06/11/96**
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