Pesticide Analytical Manual Volume I
10/97 Revisions

The following pages contain corrections or changes for PAM I. Print these pages and use them to replace the same current pages in the current PAM I 3rd edition (published 1/94, revised 9/96).

Each set of two pages is intended to appear on two sides of the same paper, but Acrobat Reader does not offer a feature that facilitates printing on both sides of the page. It may be necessary to print one page at a time and turn the paper over to print the second page on the reverse side.

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14. Appendix II, pages 15-16	Appendix II-15 and Appendix II-16	42-43

Explanations of changes:

Tables of Contents for Chapters 1, 2, and 3 now include the date of the current version for each section within the chapter.

Introduction includes revised directions for downloading PAM I from the World Wide Web; it is no longer possible to use FTP to obtain a copy of PAM I.

Section 105, page 2, is revised to clarify the formula for calculating limits of quantitation and to specify the use of methyl siloxane columns in such calculations for GLC analyses.

Pages 302-3 and 302-23 are revised to remove references to the DEGS packed GLC column, which is now considered obsolete (it is no longer commercially available).

Pages 302-27, 302-33, 302-51, and 302-57 are revised to include a new system suitability test for GLC systems used for organophosphorus residues.

Pages 302-63 through 302-70 are revised to include a statement that DEGS columns are now considered obsolete.

Appendix II, pages 15-16 are revised to remove the requirement to collect GLC data on DEGS columns.

PESTICIDE ANALYTICAL MANUAL

VOLUME I: Multiresidue Methods

U.S. Department of Health and Human Services • Public Health Service
Food and Drug Administration

PESTICIDE ANALYTICAL MANUAL VOLUME I

3rd Edition, 1994

Revised, September, 1996
Revised, October, 1997

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PESTICIDE ANALYTICAL MANUAL

INTRODUCTION

The Food and Drug Administration (FDA) is responsible under the Federal Food, Drug, and Cosmetic Act for enforcing tolerances established by the Environmental Protection Agency (EPA) for amounts of pesticide residues that may legally remain on food (including animal feed). In meeting this responsibility, FDA collects and analyzes food from commercial channels of trade for determining compliance with EPA tolerances. The residue data gathered under this regulatory monitoring program are also used for evaluating the extent and significance of pesticide residues in the food supply.

The Pesticide Analytical Manual (PAM) is published by FDA as a repository of the analytical methods used in FDA laboratories to examine food for pesticide residues for regulatory purposes.[1] The manual is organized according to the scope of the analytical methods:

Volume I contains multiresidue methods (MRMs) that are used by FDA on a routine basis, because of their efficiency and broad applicability, especially for analyzing foods of unknown pesticide treatment history.

Volume II contains methods designed for the analysis of commodities for residues of only a single compound (although some methods are capable of determining several related compounds). These methods are most often used when the likely residue is known to the chemist and/or when the residue of interest cannot be determined by common MRMs.

PAM is designed to be used by analysts experienced in trace residue analysis. All of the techniques employed are subject to potential interferences from reagents, apparatus, containers, contaminated air supply, and handling by personnel. The experienced analyst is alert for these possibilities and recognizes the need to confirm results by other techniques that measure different chemical or physical properties of the analyte.

Experienced residue analysts are aware that no report of validation in another laboratory can substitute for verification that the method does indeed work in the analyst's own laboratory. The analyst should verify method performance in each particular application by a trial of the method that includes examination of reagent and sample blanks and measurement of the recovery of added analyte. The editors invite analysts to report results of their experiences with PAM methods.

Revisions

Starting with transmittal 96-1 (9/96), revisions of PAM I have been issued in two ways: (1) changes in most manual sections will be distributed as hard (paper) copies, with symbols ▶ or ◀ marking lines that have been changed, and (2) updates to the tables

[1] 40 CFR 180.101 (c)

in Chapters 3 and 4, Appendix I, and the indices to methods, names, and CAS Registry numbers will be issued only *via* Internet. No hard copies will be distributed for the latter updated sections, but updates will be available more frequently than in the past.

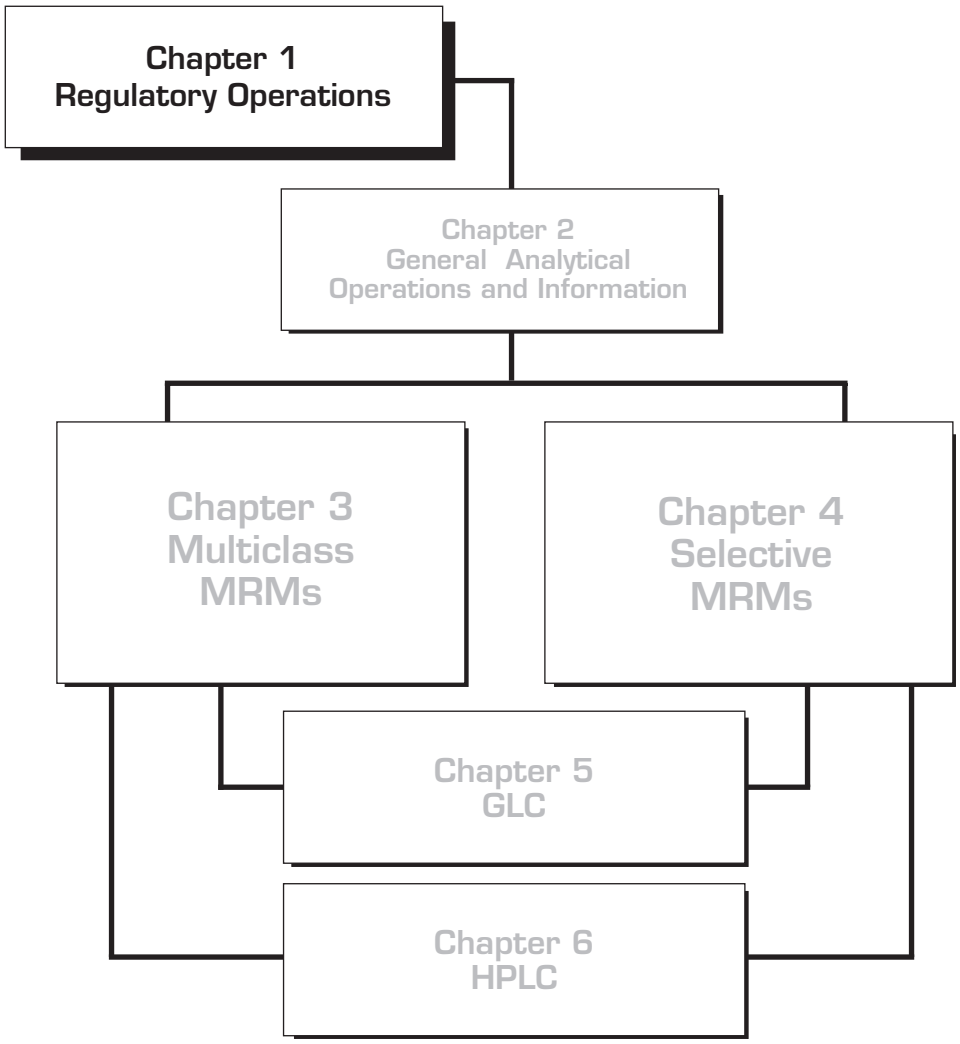
As chapter tables of contents are revised, they will include the date on which each section within the chapter was transmitted; dates associated with those sections distributed only electronically will reflect the most recent version at the time the table of contents issued.

Internet Access to PAM I Files

PAM I is now available *via* Internet as Adobe Acrobat "portable document format" (pdf) files. Pdf format permits the user to read and print the document from any computer using appropriate free software.

▶ To obtain a copy of PAM I files, go to the World Wide Web site at: http://vm.cfsan.fda.gov/~frf/pami1.html. The resulting page describes PAM and provides links to currently available files. Follow the instructions for downloading.

Adobe Acrobat Reader is required to view and print pdf files. Download a copy of this free software from Adobe's web site at http://www.adobe.com/acrobat/readstep.html. A link to that site is provided on the PAM I page. Choose the version of Acrobat Reader appropriate to your own computer system.



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105: ANALYTICAL LIMITS OF QUANTITATION

105 A: DEFINITION

FDA defines limit of quantitation (Lq) as the lowest level of residue that can be quantitated by a given method and whose identity can be confirmed in regulatory laboratories operating under routine conditions. Levels less than the Lq are defined as trace.

When MRMs are used, a separate Lq applies to each residue determined by the method because each represents a different analytical situation.

The following factors must be specified in order to define the analytical situation; only then can an Lq be calculated:

1) Analytical method used

2) Sample (matrix) type

3) Sample weight equivalent introduced to the determinative step

4) Sensitivity of the determinative step to the analyte; sensitivity is dependent on the following instrumental conditions:

   a) Determinative technique (In MRMs, the determinative step is usually GLC or HPLC; operational parameters must be defined as part of the method description.)

   b) Range of analyte weight that produces a linear detector response

   c) Overall condition of the system

   d) Amplification and/or attenuation of the detector signal

   e) Characteristics of the signal processing or recording device

   f) Chromatographic elution characteristics of the analyte

105 B: CALCULATION

FDA Lqs for each method are arrived at by (1) specifying a sample weight equivalent to be examined by the determinative step (the amount chosen must be compatible with long-term instrument stability); (2) establishing a recommended determinative step sensitivity that is stable, reproducible, and achievable by all laboratories; and (3) establishing a response equivalent to 10% of full scale deflection (FSD) on the signal-processing device as the minimum considered quantifiable and confirmable. FDA methods applied according to these guidelines are capable of analyzing for most residues at levels well below established tolerances.

Determinative step sensitivity is established by reference to a "marker compound"; *i.e.*, the instrumental parameters are adjusted to cause a specified response to a specified quantity of the marker compound. This approach makes it possible for different laboratories to achieve approximately the same Lq even though the instrument settings may be different for each. Lq for the marker compound can then be calculated with the formula below for any particular method. Lqs for all other compounds recovered through the method will vary according to the determinative step sensitivities for each.

▶ With these guidelines established, Lq for a method is calculated thus:

$$\text{ng 50\% FSD} = \text{ng analyte injected} \times \frac{\text{ng marker specified}}{\text{ng marker injected}} \times \frac{\text{marker peak height}}{\text{analyte peak height}}$$

$$\text{ng 10\% FSD} = \text{ng 50\% FSD}/5$$

$$\text{Lq} = (\text{ng 10\% FSD})/(\text{mg sample injected})$$

▶ Round the Lq result following the guidance for significant figures and reporting analytical results in Section 104, page 104-3. For general purposes, results at or below 0.010 ppm are deemed to have an Lq of 0.010 ppm.

105 C: IMPLEMENTATION

Guidelines for applying analytical methods are required to provide consistency among laboratories performing regulatory analyses. Otherwise, variations in the amount of sample equivalent injected and/or the sensitivity of the determinative step can cause different Lqs in different laboratories. Lqs that result from following FDA guidelines are adequate for the enforcement of tolerances and, in most cases, are sufficient to determine residues below the tolerance level so that data on incidence and levels of residues in foods and feeds can be collected.

The following rules are established to maintain consistent Lqs among FDA laboratories:

▶
- Establish the sensitivity recommended in each determinative step method module (*e.g.*, Section 302 DG1-DG12, Section 401 DL1). Note that the requirement for GC determinations to be based on columns of 100% methyl siloxane is in effect as of FY'98 (October 1, 1997); prior to that time, other DG modules may have been used to calculate Lq.

- Inject a volume of extract containing the equivalent sample weight recommended for each method (*e.g.*, Section 302, Determination).

- If one of the recommended specifications above cannot be achieved, or if changing one is advisable for any reason, adjust the other parameter to maintain the targeted limit of quantitation. Section 105 D describes factors that may cause problems in specific situations.

Table 105-a lists examples of Lqs that can be calculated from the recommended sample weight equivalent and determinative step sensitivity for particular PAM I methods. The list is not exhaustive but does illustrate the way in which the Lq for any method in PAM I can be calculated.

105 D: FACTORS AFFECTING TARGET LIMITS OF QUANTITATION

The following factors, individually or in combination, may reduce the certainty of quantitation and/or identification of a residue in any specific analytical situation. They may also cause the Lq to differ from the recommended limit defined by the formula above and by Table 105-a. Measures taken to compensate for one factor may trigger the influence of another.

1) Determinative step sensitivity to any particular residue. A distinct Lq applies to each residue determinable by a particular MRM, because the sensitivity of the determinative step to each compound may be different.

2) Limited detector sensitivity. Not all individual detectors are capable of reaching the sensitivity specified; in such cases, the Lq will be higher than targeted.

3) Greater detector sensitivity. Directions here recommend sensitivity at which detectors should be operated, even though some are capable of greater sensitivity. However, operation at conditions that produce recommended sensitivity may sometimes be precluded by other disadvantages in detector performance. For example, many models of ^{63}Ni electron capture detectors are not linear at conditions that produce sensitivity of 50% FSD to 1.5 ng chlorpyrifos, as is recommended for other detectors; most are linear, however, at conditions that produce 50% FSD to 0.15 ng chlorpyrifos. The rules in Section 105 C specify that, in this situation, the laboratory should operate at the greater sensitivity in order to work in a linear range, then proportionately reduce the weight of sample equivalent injected in order to maintain Lqs consistent with those achieved by other laboratories.

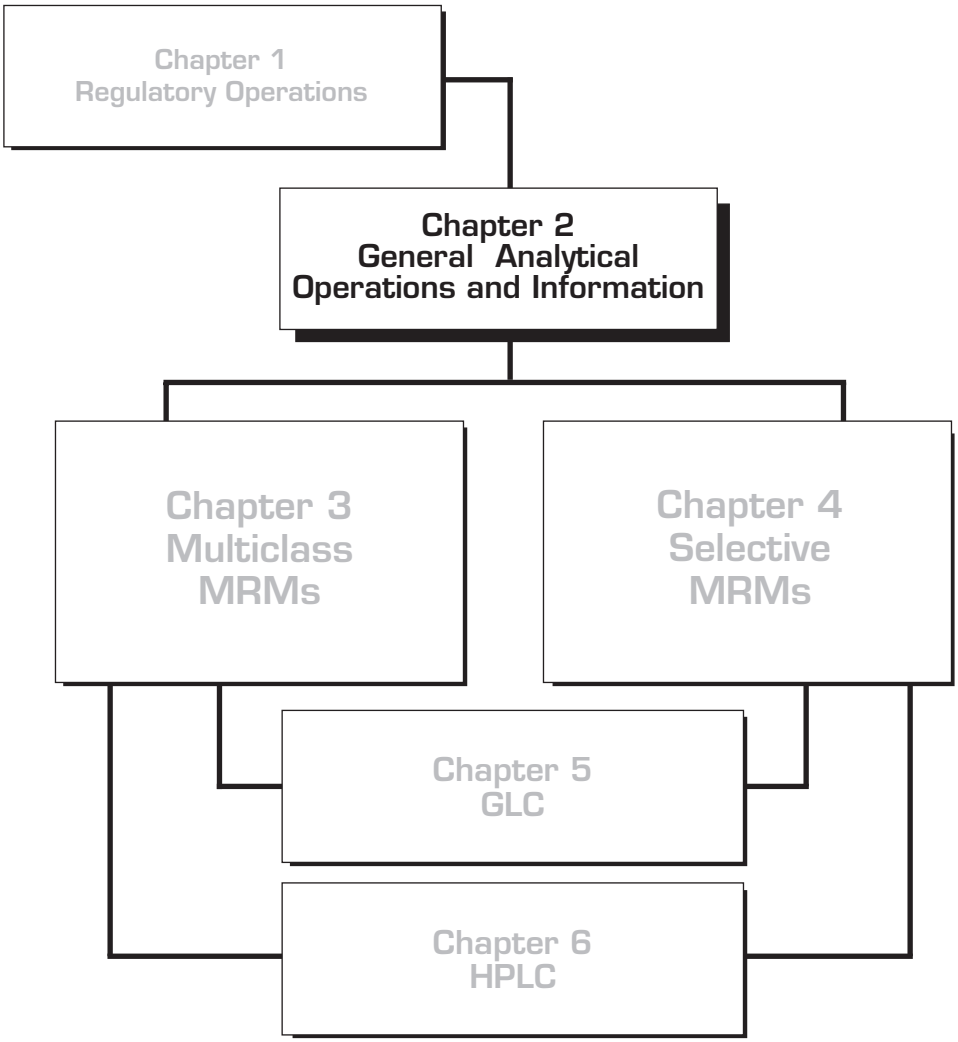
4) Other improvements that affect determinative step. Wide bore capillary GLC columns (Section 502 C) permit analytes to elute in a tighter band than was possible with packed column chromatography. When detector response is measured in terms of peak height, use of capillary columns results in an apparent improvement of response. Injection of a smaller amount of equivalent sample, as directed in Section 105 C, is appropriate and, at the same time, beneficial to the longevity of the column.

5) Excessive interferences from sample co-extractives. Interferences from sample co-extractives raise the Lq of a method by masking the detector response to the residue or by preventing injection of the specified sample equivalent without undesirable damage to the system. Additional procedures to clean up the sample extract prior to determination may improve the Lq by removing these interferences.

Table 105-a: Examples of Method Specifications Used to Calculate Lqs

PAM I Method[1]		Recommended Mg Injected	Recommended Sensitivity[2]	Lq (marker compound)[3]
302 E1+DG2 (FPD-P)		20 mg	1.5 ng chlorpyrifos	0.015 ppm chlorpyrifos
302 E3+C1+DG3 (ElCD-X)		20 mg	1.5 ng chlorpyrifos	0.015 ppm chlorpyrifos
302+E1+C3+DL1		116 mg	10 ng carbofuran	0.017 ppm carbofuran
303 E1+C1+DG1 (EC)	OR	20 mg 2 mg	1.5 ng chlorpyrifos 0.15 ng chlorpyrifos	0.015 ppm chlorpyrifos 0.015 ppm chlorpyrifos
304 E4+C2+DG1 (EC)		10 mg (cheese with 30% fat)	1.5 ng chlorpyrifos	0.03 ppm chlorpyrifos, whole product basis
401 E1+C1+DL1		200 mg	10 ng carbofuran	0.01 ppm carbofuran
402 E1+C1+DG3 (fatty foods)		5 mg Eluate 1	1.5 ng chlorpyrifos (0.2 ng PCP methyl ether)	0.008 ppm PCP methyl ether
		10 mg Eluate 2	1.5 ng chlorpyrifos (0.5 ng 2,4,5-T methyl ester)	0.01 ppm 2,4,5-T methyl ester
402 E2+C1+DG3 (nonfatty foods)		10 mg Eluate 1	1.5 ng chlorpyrifos (0.2 ng PCP methyl ether)	0.004 ppm PCP methyl ether
		20 mg Eluate 2	1.5 ng chlorpyrifos (0.5 ng 2,4,5-T methyl ester)	0.005 ppm 2,4,5-T methyl ester
403 E1+C1+DL3		800 mg	40 ng diuron	0.01 ppm diuron
404 E1+DL5		125 mg	62.5 ng MBC	0.1 ppm MBC
404 E1+DL7		125 mg	6.25 ng thiabendazole (fluorescence detector)	0.01 ppm thiabendazole

[1] Parenthetical codes indicate the detector used in the GLC determinative step.
[2] Ng marker compound that causes detector response of 50% FSD; where residues targeted by the method are different from the marker compound, weight of example target that caused 50% FSD is also listed.
[3] Calculated by formula in Section 105 B; note that sensitivity is divided by 5 to produce ng causing 10% FSD.



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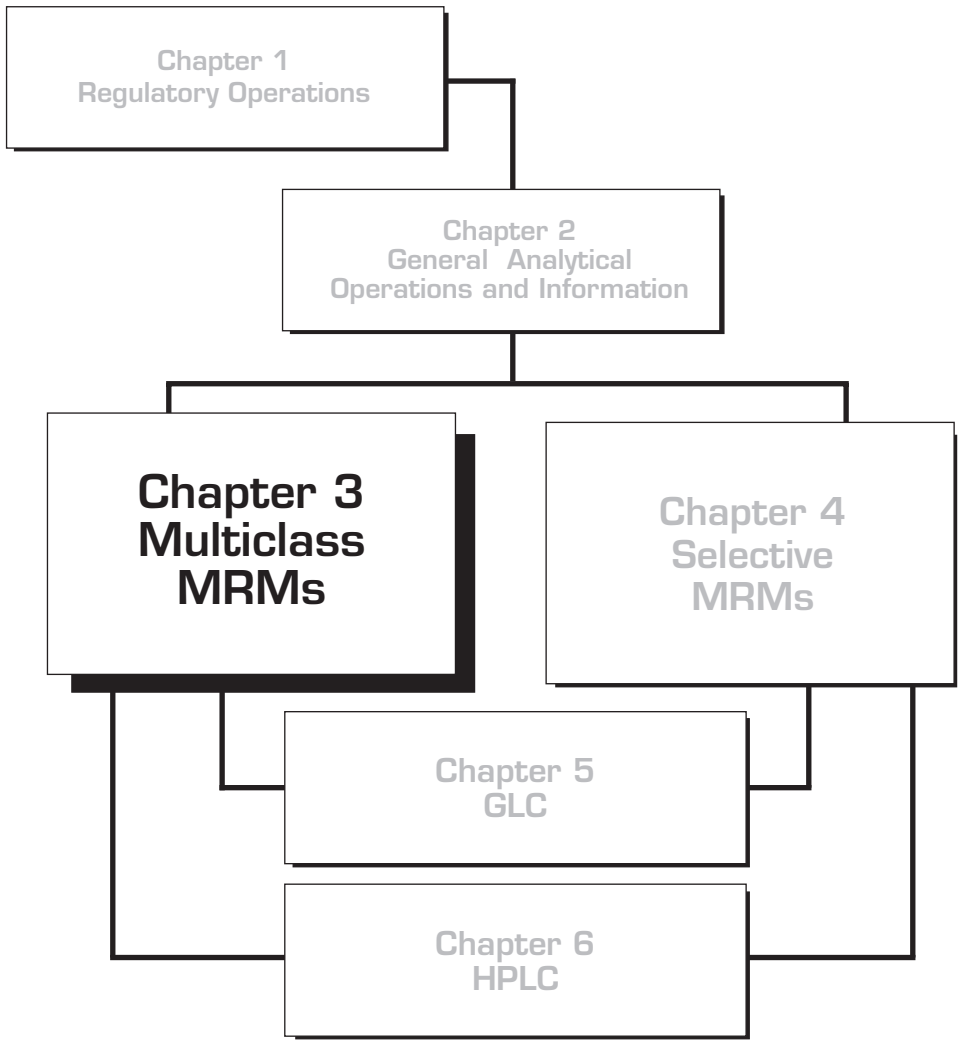

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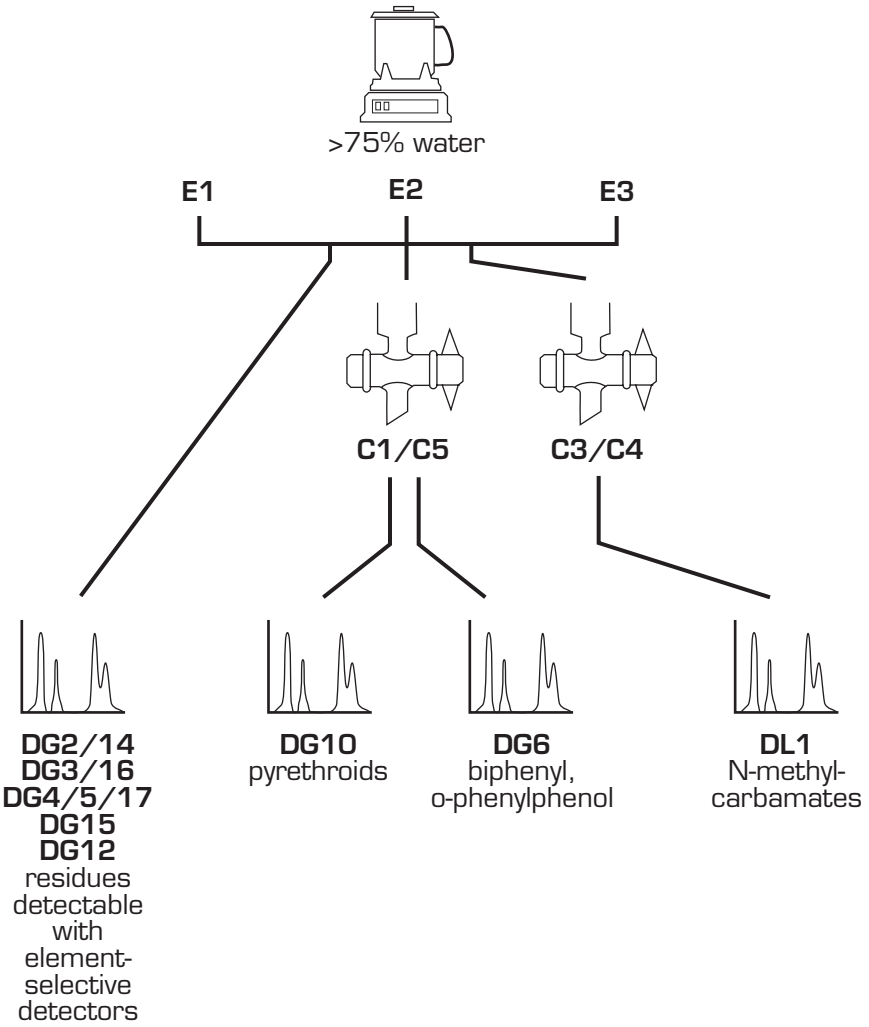
DG20	(p. 302-63)	GLC, DEGS column, 180°, FPD-P	polar residues with phosphorus
DG21	(p. 302-65)	GLC, DEGS column, 180°, FPD-S	polar residues with sulfur
DG22	(p. 302-67)	GLC, DEGS column, 180°, ElCD-X	polar residues with halogen
DG23	(p. 302-69)	GLC, DEGS column, 180°, N/P detector	polar residues with nitrogen or phosphorus
DL1	(p. 401-9)	HPLC, post-column hydrolysis and derivatization, fluorescence detection	N-methylcarbamates

Figure 302-a
Recommended Approach: Nonfatty Foods



◀

VALIDATION

Many combinations of method modules are possible. The following combinations have undergone interlaboratory validation and are recommended for use:

E1 + DG2, DG3

Validation report:

Sawyer, L.D. (1985) *J. Assoc. Off. Anal. Chem.* **68**, 64-71. Collaborative study leading to AOAC official final action status for acephate, α-BHC, chlorpyrifos, dieldrin, monocrotophos, and omethoate in lettuce, strawberries, and tomatoes.

AOAC official method reference: *Official Methods of Analysis of the AOAC* (1990) 15th ed., 985.22.

E1 + C3 + DL1

Validation report:

Pardue, J.R. (April 1987) "Recoveries of N-Methyl Carbamates Using a Combination of the Luke (PAM I, 232.4) and Krause (PAM I, 242.24b, 242.25) Procedures," LIB 3138, FDA, Rockville, MD

E2 + C1 + [temperature programmed GLC systems equivalent to] DG1, DG7, DG10, and DG16

Validation report:

Griffitt, K.R., and Szorik, M.M. (Sept 1989) "The Analysis of 127 Total Diet Items for Chlorinated Residues Using Luke/Solid Phase Extracts," LIB 3366, FDA, Rockville, MD

DETERMINATION

Inject concentrated extract equivalent to 20 mg (whole high moisture product) into the following GLC systems for determination of residues. (Although AOAC collaborative study for this method involved injection of 12 mg sample equivalent, experience since then has proven that GLC systems can tolerate routine injections equivalent to 20 mg of most nonfatty foods.)

Extract not cleaned up prior to determination:

DG2 or DG14	organophosphorus residues; large amounts of sulfur may interfere
DG3 or DG16	organohalogen residues
DG4 or	organonitrogen residues; selective to nitrogen, but co-extractives may contain nitrogen
DG5 or DG17	organonitrogen and organophosphorus residues
DG15	organosulfur residues; large amounts of phosphorus may interfere ◀
DG12	late eluting organohalogen residues, especially pyrethroids

Additional recommended determinations:

Extract not cleaned up prior to determination:

DG8	early eluting organophosphorus residues
DG11	late eluting organophosphorus residues
DG9	early eluting organohalogen residues

Extract cleaned up on Florisil column, C1 or C5:

DG1 or DG13	residues with halogen, sulfur, or other moieties
DG7	early eluting residues with halogen, sulfur, or other moieties
DG10	late eluting residues, especially synthetic pyrethroids
DG6	o-phenylphenol and biphenyl

Inject concentrated extract equivalent to about 58-116 mg (whole high moisture product) cleaned up by C3 (charcoal/Celite column) or C4 (C-18 cartridge) into following HPLC system:

DL1	N-methylcarbamates (determinative step described in Section 401)

For accurate quantitation, reference standards should be dissolved in same solvent as concentrated extract, only peaks >10% FSD should be measured, and peak sizes of residue and reference standard should match within ±25%.

See Chapter 5 for additional information about operation of GLC systems; Section 504 provides information about quantitation of residues.

See Chapter 6 for additional information about operation of HPLC systems; Section 606 provides information about quantitation of residues.

See Section 205 for additional information about reference standards.

See Section 104 for additional information about reporting residues and determining compliance with regulations.

See Section 105 for additional information about analytical limits of quantitation.

CONFIRMATION

After residues have been tentatively identified and quantitated by comparison to appropriate reference standards, confirm identity according to principles discussed in Section 103. Use appropriate tables of data (PESTDATA, tables accompanying each method, Index to Methods) to choose the most appropriate determinative steps and/or alternative methods for confirmation.

DG2 GLC, 100% METHYL SILOXANE, 200° C, FPD-P

Applicability

Determinative step is applicable to residues containing phosphorus. It is particularly useful for residues such as organophosphate pesticides.

Column

Wide bore capillary, 30 m × 0.53 mm id, coated with 100% methyl substituted polysiloxane liquid phase, 1-1.5 µm film thickness, bonded and cross-linked. For example, DB-1; see Table 502-a for equivalents. See Section 502 C, Recommended Operating Procedure for Wide Bore Columns.

Column Operating Conditions:

200° C isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of ethion is 2.56±0.05.

Carrier gas: helium; adjust flow rate so that chlorpyrifos elutes in about 4.0±0.5 min (about 20 mL/min).

Injector temperature: 220-250° C

Detector

Flame photometric, phosphorus mode (FPD-P)

Detector Operating Conditions:

225-250° C

See Section 503 C for other information about FPD operation.

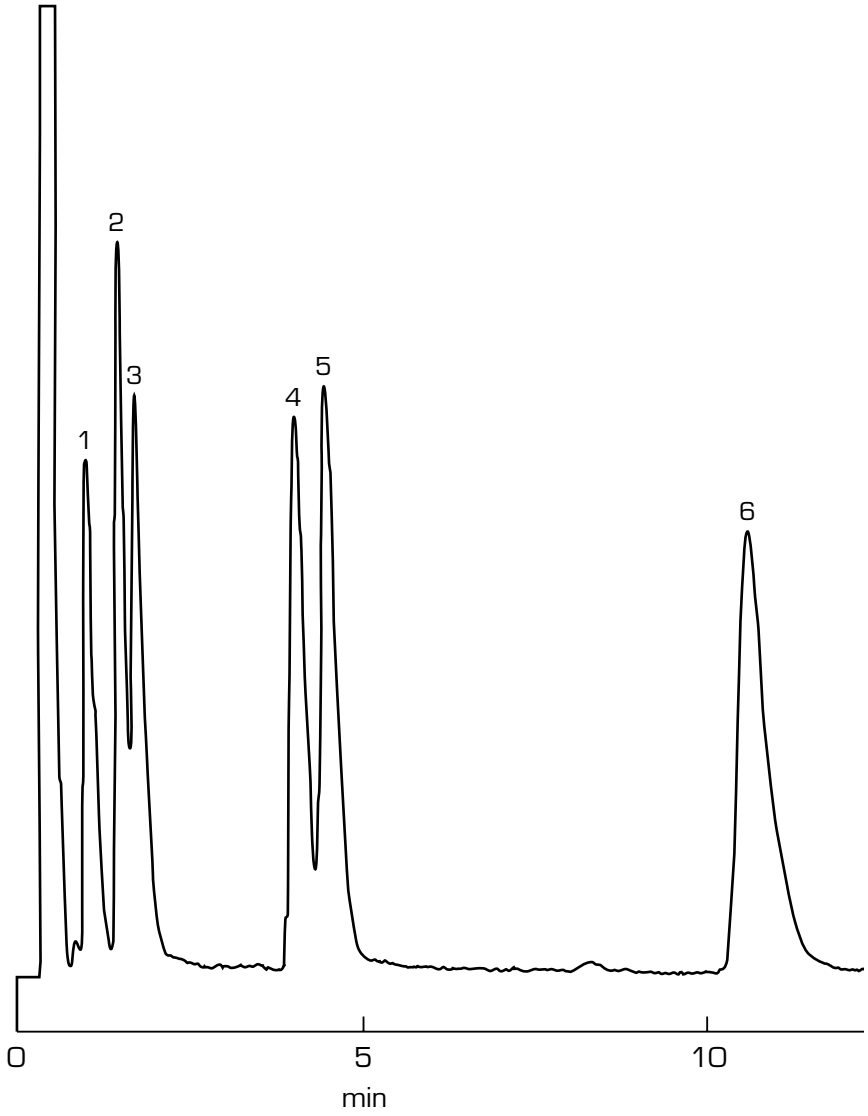
Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

A properly functioning system will give a response to 1.5 ng omethoate of ≥50% FSD. ◀

Other Considerations

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA (many data in PESTDATA were collected using equivalent packed column).

Example chromatogram is on next page.



DG2

Chromatogram of: 1) 0.85 ng acephate, 2) 1.73 ng omethoate, 3) 0.68 ng monocrotophos, 4) 1.30 ng malathion, 5) 1.27 ng chlorpyrifos, and 6) 1.26 ng ethion at the conditions described; helium carrier gas flow was 15 mL/min, with 15 mL/min make-up gas being added before the detector. Detector gas flows: 100 mL/min hydrogen, 130 mL/min air.

DG5 GLC, 100% METHYL SILOXANE, 200° C, N/P

Applicability

Determinative step is applicable to residues containing nitrogen. It is particularly useful for residues such as triazines and triazoles.

Column: Wide bore capillary, 30 m × 0.53 mm id, coated with 100% methyl substituted polysiloxane liquid phase, 1-1.5 µm film thickness, bonded and cross-linked. For example, DB-1; see Table 502-a for equivalents. See Section 502 C, Recommended Operating Procedure for Wide Bore Columns.

Column Operating Conditions:

200° C isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of ethion is 2.56±0.05.

Carrier gas: helium; adjust flow rate so that chlorpyrifos elutes in about 4.0±0.5 min (about 20 mL/min).

Injector temperature: 220-250° C

Detector

Alkali bead detector, nitrogen selective (N/P)

Detector Operating Conditions:

250° C

See Section 503 E for other information about N/P detector operation.

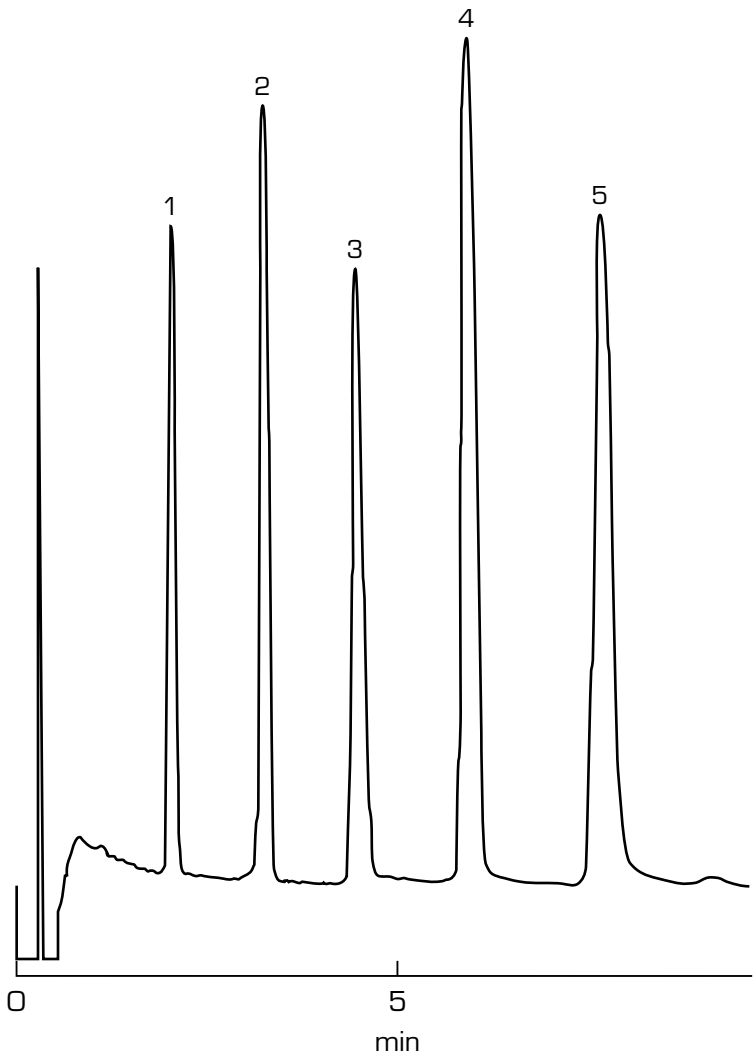
Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

A properly functioning system will give a response to 1.5 ng omethoate of ≥50% FSD. ◀

Other Considerations

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA (many data in PESTDATA were collected using equivalent packed column).

Example chromatogram is on next page.



DG5

Chromatogram of: 1) 1.0 ng atrazine, 2) 7.5 ng carbaryl, 3) 1.5 ng chlorpyrifos, 4) 2.5 ng procyazine, and 5) 5.0 ng imazalil at the conditions described.

DG14 GLC, 50% PHENYL, 50% METHYL SILOXANE, 200° C, FPD-P

Applicability

Determinative step is applicable to residues containing phosphorus. It is particularly useful for residues such as organophosphate pesticides.

Column

Wide bore capillary, 30 mm × 0.53 mm id, coated with 50% phenyl, 50% methyl substituted polysiloxane liquid phase, 1-1.5 µm film thickness, bonded and cross-linked. For example, DB-17; see Table 502-a for equivalents. See Section 502 C, Recommended Operating Procedure for Wide Bore Columns.

Column Operating Conditions:

200° C, isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of ethion is 3.36±0.07.

Carrier gas: helium; adjust flow rate so that chlorpyrifos elutes in about 4±0.5 min (about 20 mL/min).

Injector temperature: 250° C

Detector

Flame photometric, phosphorus mode (FPD-P)

Detector Operating Conditions:

225-250° C

See Section 503 C for other information about FPD operation.

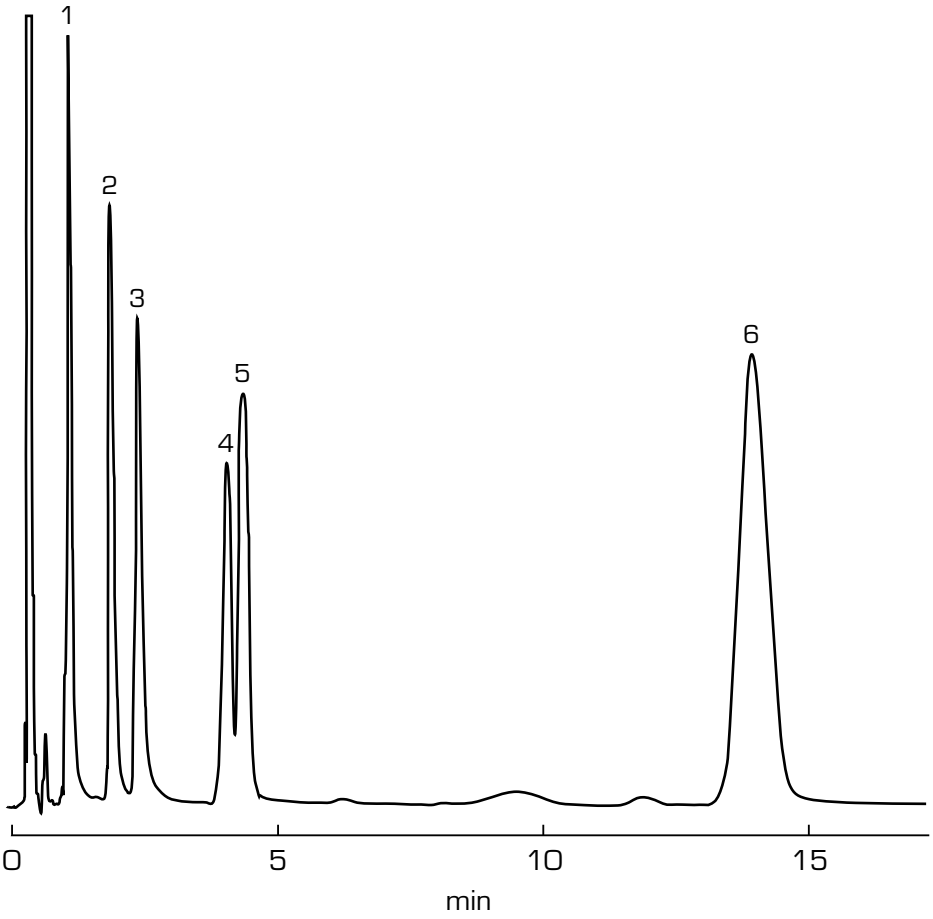
Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

A properly functioning system will give a response to 1.5 ng omethoate of ≥50% FSD. ◀

Other Considerations

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA (many data in PESTDATA were collected using equivalent packed column).

Example chromatogram is on next page.



DG14

Chromatogram of: 1) 1.0 ng acephate, 2) 1.5 ng omethoate, 3) 1.0 ng monocrotophos, 4) 1.0 ng pirimiphos-methyl, 5) 1.0 ng chlorpyrifos, and 6) 3.0 ng ethion at the conditions described.

DG17 GLC, 50% PHENYL, 50% METHYL SILOXANE, 200° C, N/P

Applicability

Determinative step is applicable to residues containing nitrogen. It is particularly useful for residues such as triazines, triazoles, and THPI (captan metabolite).

Column

Wide bore capillary, 30 m m × 0.53 mm id, coated with 50% phenyl, 50% methyl substituted polysiloxane liquid phase, 1-1.5 µm film thickness, bonded and cross-linked. For example, DB-17; see Table 502-a for equivalents. See Section 502 C, Recommended Operating Procedure for Wide Bore Columns.

Column Operating Conditions:

200° C, isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of ethion is 3.36±0.07.

Carrier gas: helium; adjust flow rate so that chlorpyrifos elutes in about 4±0.5 min (about 20 mL/min).

Injector temperature: 250° C

Detector

Alkali bead detector, nitrogen selective (N/P)

Detector Operating Conditions:

250° C

3.7±0.1 mL/min hydrogen and 110 mL/min air

See Section 503 E for other information about N/P detector operation.

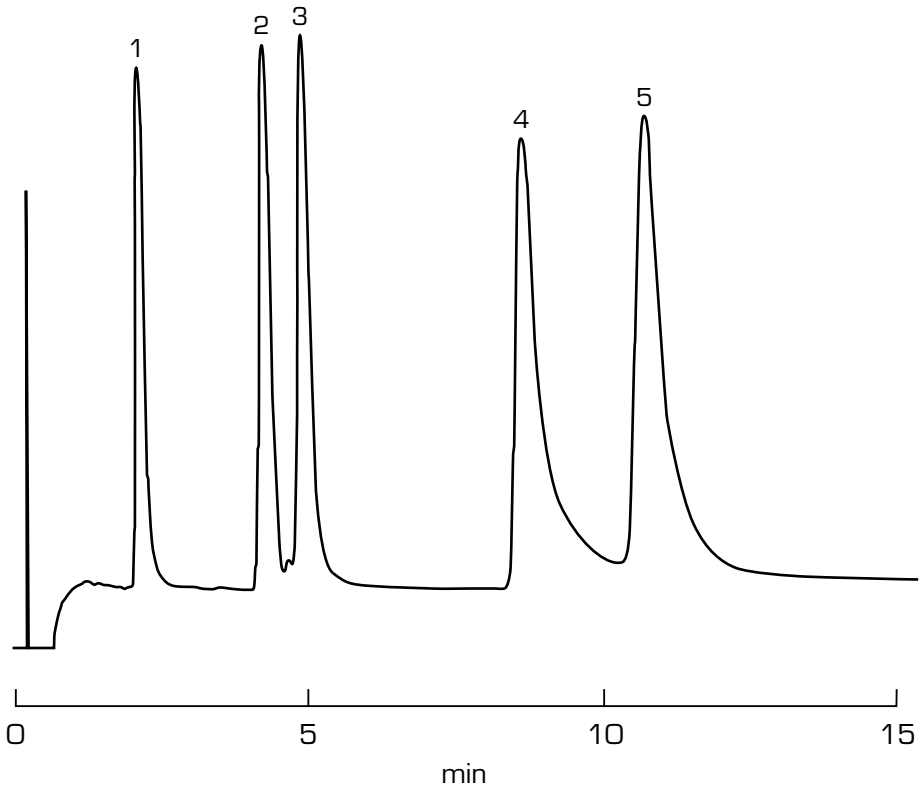
Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

A properly functioning system will give a response to 1.5 ng omethoate of ≥50% FSD. ◀

Other Considerations

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA (many data in PESTDATA were collected using equivalent packed column).

Example chromatogram is on next page.



DG17

Chromatogram of: 1) 1.5 ng atrazine, 2) 1.5 ng chlorpyrifos, 3) 15.0 ng carbaryl, 4) 10.0 ng imazalil, and 5) 5.0 ng procyazine at the conditions described.

DG20 GLC, DEGS, 180° C, FPD-P

NOTICE: Because DEGS column packing is no longer available commercially, FDA laboratories may use it for confirmatory analyses only as of Nov., 1997. ◀

Applicability

Determinative step is applicable to residues containing phosphorus. It is particularly useful for residues such as polar organophosphate pesticides and their metabolites.

Column

4' × 2 mm id 2% DEGS (stabilized) on Chromosorb W AW, 80/100 mesh. Packing is no longer commercially available but is still used in some laboratories.

Column Operating Conditions:

180° C, isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of parathion is 2.50±0.05.

Carrier gas: nitrogen/helium; adjust flow rate so that chlorpyrifos elutes in about 2-2.5 min (about 30 mL/min).

Injector Temperature: 190° C (not more than 10° C above column temperature)

Column Conditioning: With column disconnected from detector, degas column with nitrogen at 60 mL/min for 0.5 hr. After degassing, program temperature at 1-2° C/min to 230° C. Condition with carrier flow at 230° C for 16 hr.

Detector

Flame photometric, phosphorus mode (FPD-P)

Detector Operating Conditions:

225-250° C

See Section 503 C for other information about FPD operation.

Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

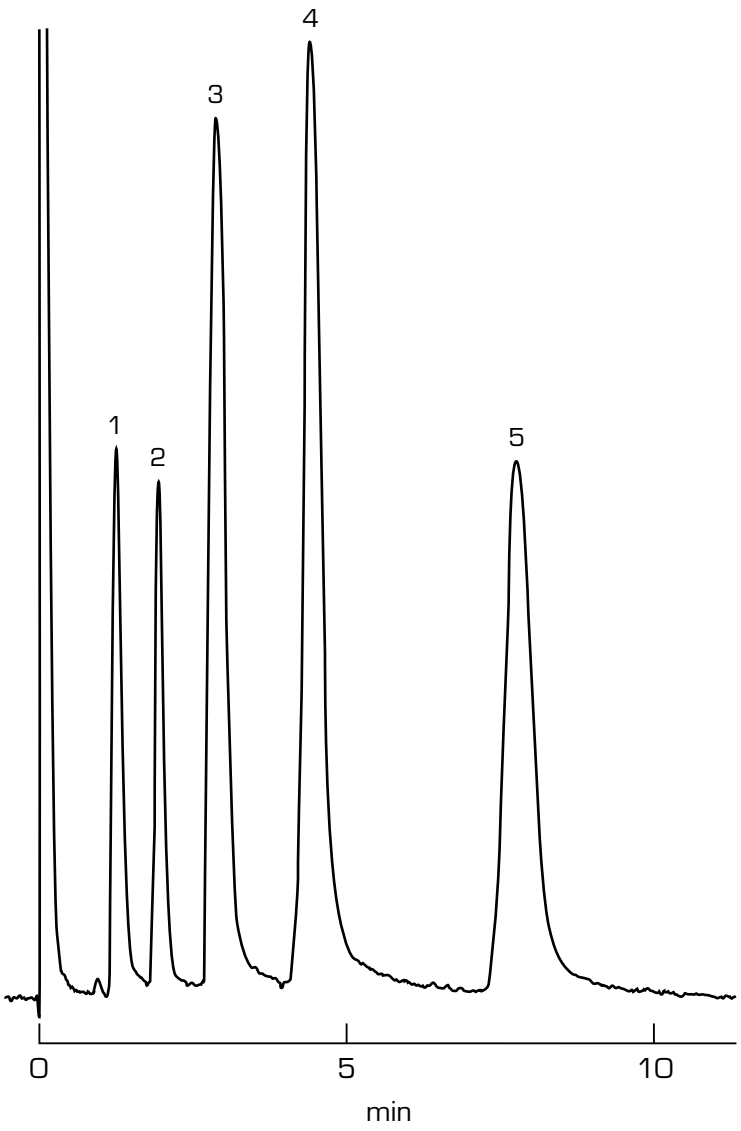
Other Considerations

When using a DEGS column, it is necessary to ascertain that polar chemicals are chromatographing properly. Adjust the system of DEGS column and FPD-P detector to result in a peak of 50% FSD for 1.5 ng chlorpyrifos. A DEGS column on which polar chemicals chromatograph properly will produce the same size peak in response to ≤8 ng monocrotophos. Do not use a DEGS column on which monocrotophos cannot be seen.

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA.

DEGS columns may not tolerate injection of extracts from fatty foods; use caution if such determination is necessary.

Example chromatogram is on next page.



DG20

Chromatogram of: 1) 0.73 ng methamidophos, 2) 1.35 ng chlorpyrifos, 3) 3.72 ng acephate, 4) 7.12 ng omethoate, and 5) 5.40 ng monocrotophos.

DG21 GLC, DEGS, 180° C, FPD-S

NOTICE: Because DEGS column packing is no longer available commercially, FDA laboratories may use it for confirmatory analyses only as of Nov., 1997. ◀

Applicability

Determinative step is applicable to residues containing sulfur. It is particularly useful for residues such as polar organothiophosphate pesticides and their metabolites.

Column

4' × 2 mm id 2% DEGS (stabilized) on Chromosorb W AW, 80/100 mesh. Packing is no longer commercially available but is still used in some laboratories.

Column Operating Conditions:

180° C, isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of parathion is 2.50±0.05.

Carrier gas: nitrogen/helium; adjust flow rate so that chlorpyrifos elutes in about 2-2.5 min (about 30 mL/min).

Injector Temperature: 190° C (not more than 10° C above column temperature)

Column Conditioning: With column disconnected from detector, degas column with nitrogen at 60 mL/min for 0.5 hr. After degassing, program temperature at 1-2° C/min to 230° C. Condition with carrier flow at 230° C for 16 hr.

Detector

Flame photometric, sulfur mode (FPD-S)

Detector Operating Conditions:

225-250° C

See Section 503 C for other information about FPD operation.

Set detector electronics (amplification, attenuation) to produce greatest possible response (50% full scale deflection [FSD] to 15 ng chlorpyrifos is reasonable).

Other Considerations

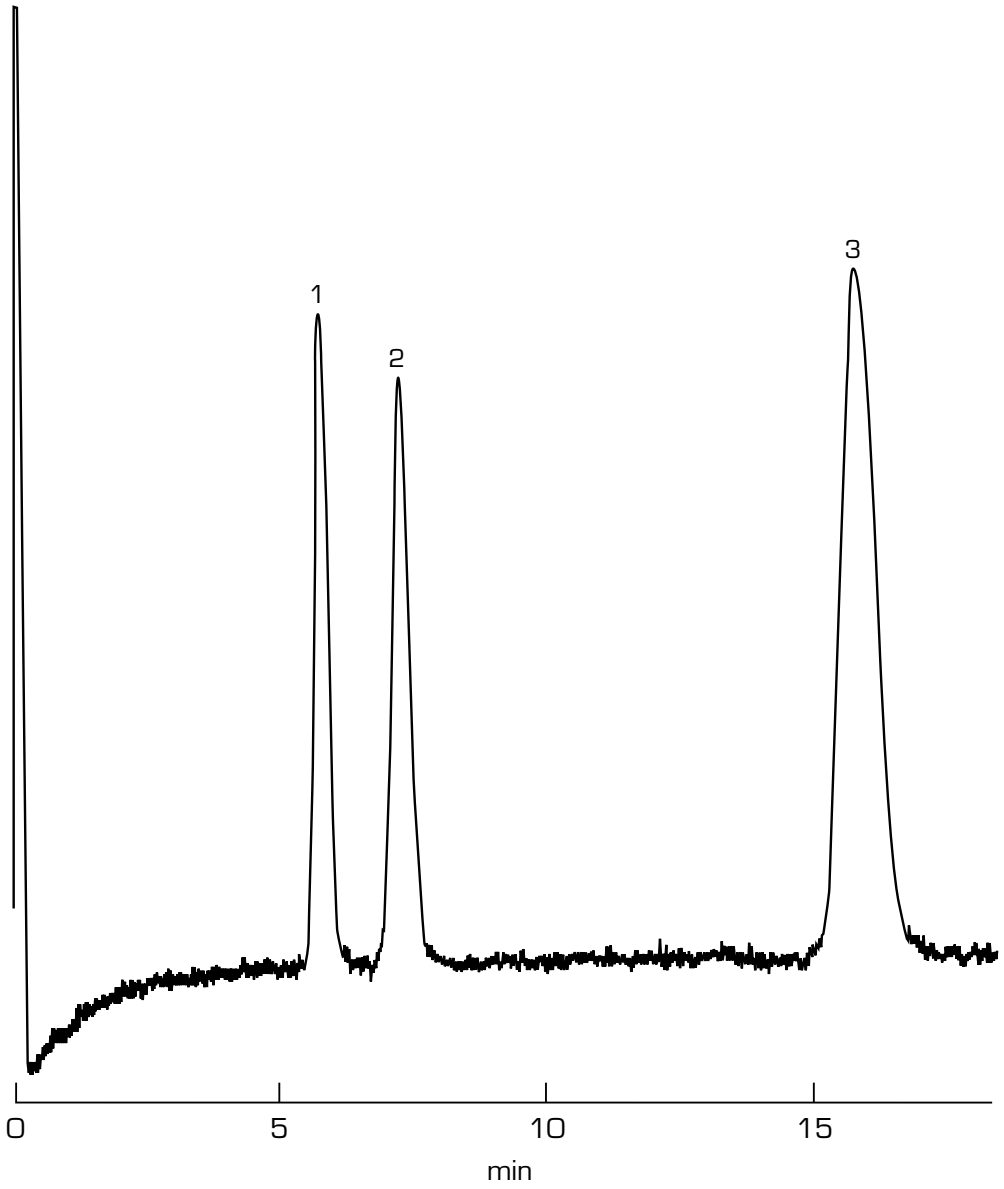
When using a DEGS column, it is necessary to ascertain that polar chemicals are chromatographing properly. Adjust the system of DEGS column and FPD-P detector to result in a peak of 50% FSD for 1.5 ng chlorpyrifos. A DEGS column on which polar chemicals chromatograph properly will produce the same size peak in response to ≤8 ng monocrotophos. Do not use a DEGS column on which monocrotophos cannot be seen.

Detector is not linear; quantitation of residues may be calculated from calibration curve (response *vs* amount injected).

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA.

DEGS columns may not tolerate injection of extracts from fatty foods; use caution if such determination is necessary.

Example chromatogram is on next page.



DG21

Chromatogram of: 1) 14.4 ng ethofumesate, 2) 12.6 ng metribuzin, and 3) 48.8 ng propargite at the conditions described, except that the detector was at 200° C. Using this system, 1.64 ng chlorpyrifos caused 37% FSD response.

DG22 GLC, DEGS, 180° C, ELCD-X

NOTICE: Because DEGS column packing is no longer available commercially, FDA laboratories may use it for confirmatory analyses only as of Nov., 1997. ◀

Applicability

Determinative step is applicable to residues containing halogen. It is particularly useful for residues such as oxadiazon, which co-elutes with dieldrin on some other columns. This system also separates p,p′ -DDE from dieldrin when they occur in the same extract, *e.g.*, analysis of root crops with Section 302.

Column

4′ × 2 mm id 2% DEGS

Column Operating Conditions:

180° C, isothermal

Carrier gas: nitrogen/helium; adjust flow rate so that chlorpyrifos elutes in about 2-2.5 min (about 30 mL/min).

Injector Temperature: 190° C (not more than 10° C above column temperature)

Column Conditioning: With column disconnected from detector, degas column with nitrogen at 60 mL/min for 0.5 hr. After degassing, program temperature at 1-2° C/min to 230° C. Condition with carrier flow at 230° C for 16 hr.

Detector

Electroconductivity, halogen mode (ElCD-X)

Detector Operating Conditions:

base temperature 250° C, furnace temperature 900° C (or as specified in operating manual)

Reactor gas: hydrogen, flow as required by specific detector model; see operating manual

See Section 503 D for other information about ElCD operation.

Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

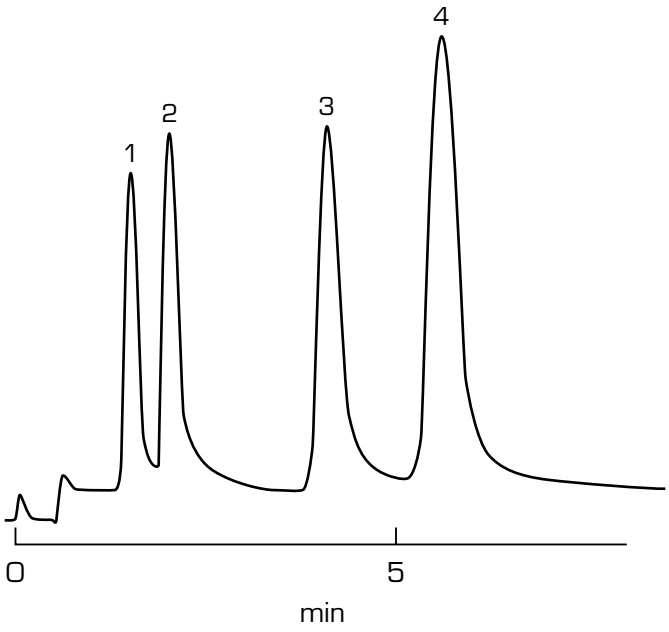
Other Considerations

When using a DEGS column, it is necessary to ascertain that polar chemicals are chromatographing properly. Adjust the system of DEGS column and FPD-P detector to result in a peak of 50% FSD for 1.5 ng chlorpyrifos. A DEGS column on which polar chemicals chromatograph properly will produce the same size peak in response to ≤8 ng monocrotophos. Do not use a DEGS column on which monocrotophos cannot be seen.

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA.

DEGS columns may not tolerate injection of extracts from fatty foods; use caution if such determination is necessary.

Example chromatogram is on next page.



DG22

Chromatogram of: 1) 1.11 ng trichloronat, 2) 1.71 ng ronnel oxygen analog, 3) 4.06 ng oxadiazon, and 4) 4.59 ng procymidone at the conditions described.

DG23 GLC, DEGS, 180° C, N/P

NOTICE: Because DEGS column packing is no longer available commercially, FDA laboratories may use it for confirmatory analyses only as of Nov., 1997. ◀

Applicability

Determinative step is applicable to residues containing nitrogen. It is particularly useful for polar residues such as carbamates and organophosphate pesticide metabolites.

Column

4′ ×2 mm id 2% DEGS (stabilized) on Chromosorb W AW, 80/100 mesh. Packing is no longer commercially available but is still used in some laboratories.

Column Operating Conditions:

180° C, isothermal; if necessary, adjust temperature so that relative retention time to chlorpyrifos (rrt_c) of parathion is 2.50±0.05.

Carrier gas: nitrogen/helium; adjust flow rate so that chlorpyrifos elutes in about 2-2.5 min (about 30 mL/min).

Injector Temperature: 190° C (not more than 20° C above column temperature)

Column Conditioning: With column disconnected from detector, degas column with nitrogen at 60 mL/min for 0.5 hr. After degassing, program temperature at 1-2° C/min to 230° C. Condition with carrier flow at 230° C for 16 hr.

Detector

Alkali bead detector, Nitrogen Selective (N/P)

Detector Operating Conditions:

250° C

See Section 503 E for other information about N/P detector operation.

Set detector electronics (amplification, attenuation) so that response to 1.5 ng chlorpyrifos is 50% full scale deflection (FSD).

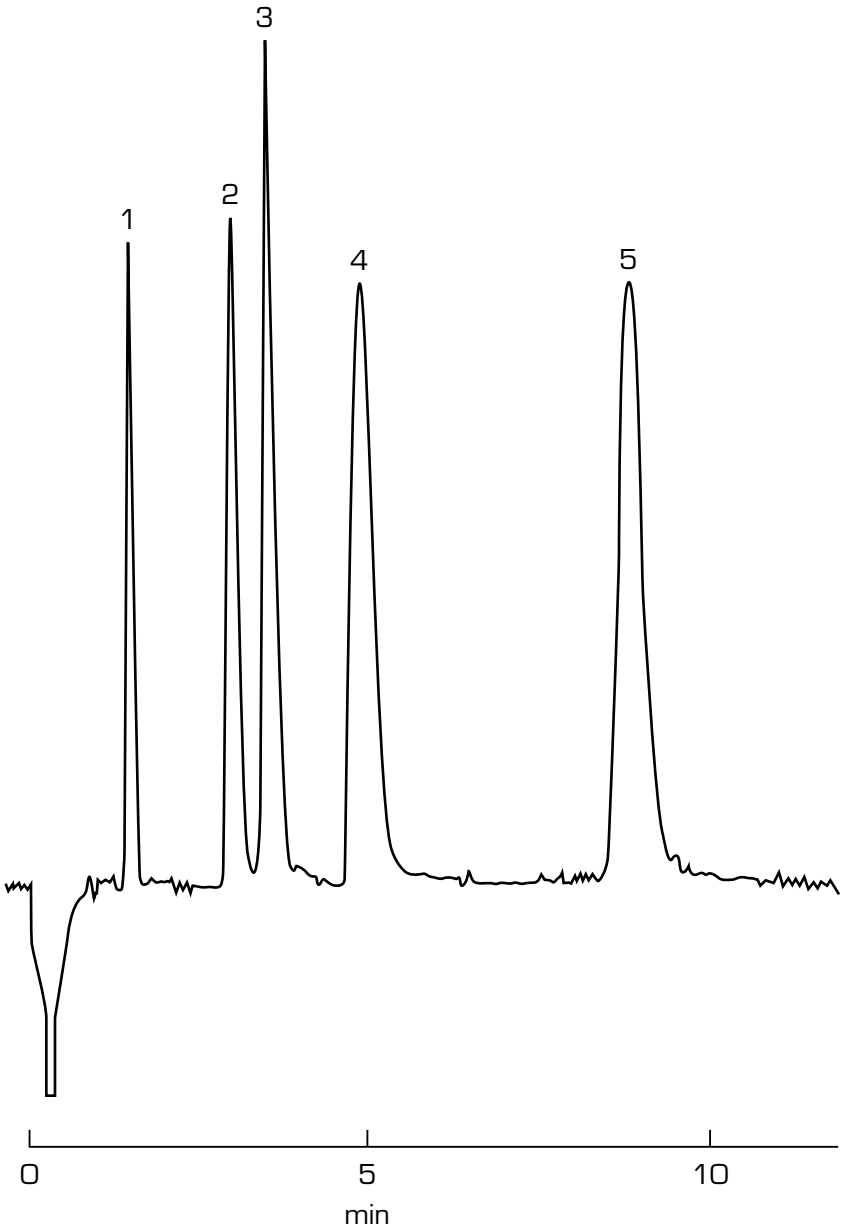
Other Considerations

When using a DEGS column, it is necessary to ascertain that polar chemicals are chromatographing properly. Adjust the system of DEGS column and FPD-P detector to result in a peak of 50% FSD for 1.5 ng chlorpyrifos. A DEGS column on which polar chemicals chromatograph properly will produce the same size peak in response to ≤8 ng monocrotophos. Do not use a DEGS column on which monocrotophos cannot be seen.

Rrt_cs and ng required to cause 50% FSD response are listed in Appendix I, PESTDATA.

DEGS columns may not tolerate injection of extracts from fatty foods; use caution if such determination is necessary.

Example chromatogram is on next page.



DG23

Chromatogram of: 1) 1.5 ng diphenylamine, 2) 1.5 ng chlorpyrifos, 3) 2.05 ng aminocarb, 4) 3.25 ng oxythioquinox, and 5) 7.5 ng napropamide at the conditions described.

PROTOCOL C: PROCEDURE FOR DEVELOPING GLC DATA

BACKGROUND

Methods: Section 302 DG1-DG23; GLC systems are used with Sections 302, 303, 304, and 402 methods.

Chemical Type: Applicable to chemicals that can be vaporized at temperatures about 250° C without degradation. Most pesticides and their related chemicals that meet this criterion can be chromatographed and detected by at least one of the GLC systems DG1-DG23.

PAM I Tables: Appendix I (PESTDATA)

DATA DEVELOPMENT

For each GLC DG module tested:

- Dissolve reference standard in pesticide grade solvent to prepare stock standard solution. Isooctane is preferred, but acetone may be required for dissolution.
- Set up GLC system as described in specified DG module (Section 302). Check rrts of marker compounds and adjust column temperature to match conditions specified.
- Inject aliquots of test solution into GLC.
- Calculate retention time (relative to marker compound specified in DG module).
- Calculate ng standard that causes 50% FSD response. Do not inject >1000 ng (1 μg).
- Test chemical on one or more of these systems:

  Level I:

  All chemicals:

  DG 1 100% methyl siloxane (*e.g.*, DB-1), 200° C, EC

  DG13 50% phenyl, 50% methyl siloxane(*e.g.*, DB-17), 200° C, EC

  DG18 50% cyanopropylphenyl, 50% methyl siloxane (*e.g.*, DB-225), 200° C, EC

  Chemicals containing halogen:

  DG 3 100% methyl siloxane (*e.g.*, DB-1), 200° C, ElCD-X

  DG16 50% phenyl, 50% methyl siloxane (*e.g.*, DB-17), 200° C, ElCD-X

Chemicals containing phosphorus:

DG 2 100% methyl siloxane (*e.g.*, DB-1), 200° C, FPD-P

DG14 50% phenyl, 50% methyl siloxane (*e.g.*, DB-17), 200° C, FPD-P

DG19 50% cyanopropylphenyl, 50% methyl siloxane (*e.g.*, DB-225), 200° C, FPD-P

▶

Chemicals containing sulfur:

DG15 50% phenyl, 50% methyl siloxane (*e.g.*, DB-17), 200° C, FPD-S

▶

Chemicals containing nitrogen:

DG 4 100% methyl siloxane (*e.g.*, DB-1), 200° C, ElCD-N

DG 5 100% methyl siloxane (*e.g.*, DB-1), 200° C, N/P

DG17 50% phenyl, 50% methyl siloxane (*e.g.*, DB-17), 200° C, N/P

▶

Chemicals with no heteroatom to which element-selective detectors respond:

DG 6 100% methyl siloxane (*e.g.*, DB-1), 130° C, FID

Level II:

If chemical chromatographs on system described in module(s) of Level I, but rrt is <0.3, rechromatograph at lower column temperature, *e.g.*:

DG 7 100% methyl siloxane (*e.g.*, DB-1), 130° C, EC

DG 8 100% methyl siloxane (*e.g.*, DB-1), 130° C, FPD-P

DG 9 100% methyl siloxane (*e.g.*, DB-1), 130° C, ElCD-X

If chemical chromatographs on system described in module(s) of Level I, but rrt is >5.0, rechromatograph at higher column temperature, *e.g.*:

DG10 100% methyl siloxane (*e.g.*, DB-1), 230° C, EC

DG11 100% methyl siloxane (*e.g.*, DB-1), 230° C, FPD-P

DG12 100% methyl siloxane (*e.g.*, DB-1), 230° C, ElCD-X

REPORTING RESULTS

Report results for each DG module on copy of Reporting Form C. An asterisk (*) appears on form wherever name of tested chemical should be entered.