

Proceedings: NOBCCChE '94

**21st Annual National Conference
of the National Organization of
Black Chemists and Chemical Engineers
April 4-9, 1994, Atlantic City, New Jersey**

August 31, 1994

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Manuscript date: August 31, 1994

**Technical Program Chairmen: Dr. D. Inniss and Dr. J.W. Mitchell
Proceedings Committee Chairman: Dr. Bruce Harris**

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PREFACE

The 21st Annual National Conference of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers (NOBCChE) was held in Atlantic City, New Jersey, from April 4–9, 1994. The theme for the meeting was "Meeting the Global Challenge." Accordingly, the organizers, led by Conference Chair, Dr. Victor McCrary of AT&T Bell Laboratories, created an appropriate forum for attendees to consider the worldwide issues facing them in many areas of their professional lives. The meeting was highlighted by informative and interesting technical sessions, provocative special interest forums, and outstanding speeches.

Approximately 400 registered attendees took part in NOBCChE '94. In addition, the Science Bowl and Science Fair competitions attracted over 200 secondary school students and their teachers and parents, as well as attendees at the conference. Thirty-four exhibitors from all areas of private industry and governmental organizations took part in the Industrial Exhibit's recruiting efforts for this year. Therefore, approximately 600 people took part in some aspect of NOBCChE '94.

The Technical Program Committee, co-chaired by Dr. Daryl Inniss and Dr. Jim Mitchell, both of AT&T Bell Laboratories, did an excellent job in organizing a solid technical program made up of approximately 120 invited and solicited papers presented in approximately six different technical sessions and nine different technical symposia. The technical sessions encompassed the conventional areas of research, such as chemical engineering, material science, and inorganic, organic, physical, environmental, and polymer chemistry. The technical symposia included The National Institute of Standards and Technology Symposium on Technological Competitiveness, The Tennessee Valley Authority Symposium on Environmental and Industrial Analytical Chemistry, The Rohm and Haas Undergraduate Research Presentations, and the NOBCChE/American Chemical Society Joint Symposium on AIDS. Other symposia were in the areas of Biosciences and Biotechnology, Organic Chemistry in the Pharmaceutical Industry, and Environmental Science and Management. The special interest forums included a Forum for Laboratory Technicians.

The meeting was highlighted by several outstanding speeches. Of special note, Professor Shirley A. Jackson of the Department of Physics at Rutgers University and the first African-American woman to receive a doctorate from M.I.T. in any field received the Henry Hill Award. Her keynote speech was preceded by an introduction by the Honorable Christine Todd Whitman, Governor of New Jersey. Former Mayor of New York City, David N. Dinkins, gave an address at a reception on "Achieving Excellence Through Diversity: Individual and Corporate Strategies."

This meeting was also highlighted by a "Town Meeting" where graduate and undergraduate students had an opportunity to express concerns about issues facing them and how NOBCChE can assist in addressing them.

The Annual Awards Banquet was highlighted by a speech by Dr. Cecil B. Pickett, Executive Vice-President for Research Operations at Schering-Plough Research Institute. The awards and recipients were: Proctor and Gamble Graduate Fellowship, Ms. Mary E. Peek, Ph.D. candidate, Biochemistry, Georgia Institute of Technology; Eastman Kodak Dr. Theophilus Sorrell Graduate Fellowship, Mr. Reginald Parker, Ph.D. candidate, Chemical Engineering, Georgia Institute of Technology; E.I. DuPont Graduate Fellowship, Mr. James W. Ledbetter, Ph.D. candidate, Chemical Engineering, University of Illinois at Urbana-Champaign; NOBCChE Rohm and Haas Company Undergraduate Research Awards, in Chemistry Mr. Daniel J. Mindiola of Michigan State and Mr. Kawaku Williams-Ajao of Howard University, and in Chemical Engineering Ms. Michele Z. Darbeau of Howard University; NOBCChE Lawrence Livermore National Laboratory, James E. Evans Undergraduate Award in Chemistry and Chemical Engineering, Mr. Weldon Hall, San Diego,

CA. Dr. Leroy Chauffe, Chairman, Department of Chemistry, California State University, Hayward, received the NOBCCChE Outstanding Teacher Award. Dr. Dotsevi Y. Sogah, Professor of Chemistry, Cornell University, Ithaca, NY, received the NOBCCChE Percy L. Julien Award.

Congratulations on a successful NOBCCChE '94! We are hoping for similar success at NOBCCChE '95 in Los Angeles.

Bruce D. Harris, Ph.D.

Chair, Proceedings Committee, NOBCCChE

R. W. Johnson Pharmaceutical Research Institute, Spring House, Pennsylvania

ACKNOWLEDGMENTS

The publishing of the *Proceedings* for the 21st Annual National Conference of NOBCCChE involved the efforts of many people. I would like to especially thank all of the presenters who gave talks at the meeting and invested the time and effort to prepare and submit their paper for inclusion in this volume of the *Proceedings*. I acknowledge the outstanding work of the members of the Technical Program Committee for this meeting and thank them for their cooperation in bringing this endeavor to a successful conclusion. The Technical Program Committee was headed by Dr. Daryl Inniss and Dr. Jim Mitchell, both of AT&T Bell Laboratories. I thank them both for their commitment in putting together such a fine program.

As always, I extend heart-felt thanks and appreciation to the members of the Proceedings Committee for their exemplary team work and outstanding commitment to this task: Ms. Gwen Evans, Lawrence Livermore National Laboratory (LLNL); Dr. Daryl Inniss, AT&T Bell Laboratories; Dr. Tommie Royster, Eastman Kodak; and Dr. Alison Williams, Swarthmore College. I would especially like to welcome and thank two new members of the Committee: Dr. Yvette Dick-Clifton, Integrated Teachings Institute, and Dr. Victor Rodgers, University of Iowa. This is the third year the Proceedings Committee has issued the *Proceedings* for the National NOBCCChE Conference. As in the past, the exceptional efforts of the members of this committee have made a potentially overwhelming task a pleasurable experience.

I extend special thanks to Dr. Keith Guinn of AT&T Bell Laboratories for his invaluable assistance in compiling this manuscript and to Ms. Catherine Ulatowski at LLNL for typesetting the forematter for this volume. Lastly, I again express appreciation to our publisher, Kassahun Checole of Africa World Press, Inc., for his continued support and interest in this project.

Bruce D. Harris, Ph.D.

Chair, Proceedings Committee, NOBCCChE

R. W. Johnson Pharmaceutical Research Institute, Spring House, Pennsylvania

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SEQUENTIAL SOLID-PHASE EXTRACTION FOR THE DETERMINATION OF ORGANOPHOSPHORUS AND ORGANOCHLORINE PESTICIDE RESIDUES IN VEGETABLE OILS AND BUTTERFAT

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Abstract

The analysis of pesticide residues in fats and oils requires extraction and cleanup procedures to isolate the pesticides from the lipid matrix prior to gas chromatographic (GC) analysis. Diatomaceous earth columns used with reversed phase and normal phase solid phase extraction (SPE) cartridges were evaluated for the quantitative determination of a number of organophosphorus (OP) and organochlorine (OC) pesticide residues in edible vegetable oils and butter-fat. A ~2 g sample of oil or butter-fat in hexane was taken through a diatomaceous earth (Extrelut QE) column and a C-18 bonded silica (ODS) SPE cartridge resulting in the separation of the pesticides from about 98 % of the lipids. The eluate was split in half and one portion concentrated into acetone for the determination of OP pesticides by gas chromatography with flame photometric detector (GC-FPD). The other half of the eluate was passed through alumina N SPE cartridge for additional cleanup of lipid matrix in order to determine OC pesticides by GC using a electron-capture detector (ECD). Average recoveries from fortified samples were greater than 89 % for the pesticides studied.

Introduction

Separation of trace levels of pesticides from edible oils in preparation for analysis by gas chromatography requires the use of sample preparation techniques that will separate the pesticides from lipids since small amounts of lipids can cause deterioration of the column and contamination of the detector. Techniques for fat food cleanup prior to GC determination of pesticide residues have been reviewed in a recent publication (1). Three elution systems used most often with Florsil to isolate OC pesticides from extracts containing lipids were compared with another study (2). The AOAC official method of analysis for several organo-chlorine and organophosphorus pesticide residues in fat containing foods (3) uses conventional gravity flow Florisil columns to remove residual fat from sample extracts after partial cleanup by partitioning between aqueous acetonitrile and petroleum ether. These procedures are time consuming and give low

recoveries for some pesticides. Almost 1000 ml of solvent is used to extract 3 g of fats or oils in this official method.

Reversed phase liquid chromatography using semi-preparative C-18 HPLC columns was previously found to be effective for separating OP and OC pesticides from a variety of edible oils and fats (4,5). The need for relatively expensive equipment and the limited sample throughput attained with a single LC system made this approach impractical. Therefore, SPE cartridges packed with C-18 bonded silica packings were investigated as an alternative to the semi-preparative LC procedure and were successfully applied to the determination of OP pesticide residues (6). The use of commercial SPE cartridges containing silica and Florisil packings for cleanup of lipid samples prior to pesticide analysis has been reported (7-9). Several groups reported using disposable mini-columns of a macroporous Kieselgurh-type material (Extrelut QE) for the partitioning of OP pesticides into acetonitrile from hexane solution of fats (10-12). Further cleanup of OP pesticide residues from oils and fatty extracts was accomplished using SPE cartridges packed with silica and C-18. DiMuccio modified the Extrelut QE method by the addition of sulfuric acid for the determination of organochlorine pesticides (13). Milk has also been analyzed for organochlorine pesticides using the Extrelut QE column (14).

This report presents a combined Extrelut QE, reversed phase and normal phase SPE cleanup system for the determination of OP and OC pesticide residues in vegetable oils and butter-fat from a single sample solution using only about 200 ml of solvent.

Experimental

Reagents and Apparatus

(a) Solvents-Acetone, acetonitrile, dichloromethane, hexane, isooctane and methanol distilled in glass or equivalent and residue grade.

(b) Standards - Diazinon, methamidophos, acephate, chlorpyrifos, methyl parathion, azodrin, aldrin, heptachlor epoxide, dieldrin, endrin, p,p'- DDT and pp'methoxychlor reference standards were obtained from the U.S. Environmental Protection Agency (EPA), Pesticide and Industrial Chemicals Repository (Research Triangle Park, NC, 27711). **OP working standard solution** is prepared in acetone to contain approximately 0.2 µg/ml diazinon, 0.17 µg/ml methamidophos, 0.7 µg/ml chlorpyrifos and 0.2 µg/ml acephate. **OC working standard solution** is prepared in 1:1 isooctane-hexane to contain approximately 0.03 µg/ml aldrin,

0.04 $\mu\text{g/ml}$ heptachlor epoxide, 0.04 $\mu\text{g/ml}$ dieldrin, 0.04 $\mu\text{g/ml}$ endrin, 0.09 $\mu\text{g/ml}$ p,p'-DDT and 0.23 $\mu\text{g/ml}$ p,p'-methoxychlor.

(c) Extrelut QE disposable columns, 3 ml capacity (EM Science, Gibbstown, N.J. 08027).

(d) Solid-phase extraction cartridges - Sep Pak C-18, 5 g and Sep Pak Alumina, N, 5 g (Waters Assoc., Milford, Massachusetts 01757).

(e) Vacuum rotary evaporator- Buchi Rotovapor Model RE111 (Brinkmann Instruments, Inc., Westbury, N. Y. 11590)

(f) Gas chromatographs.

For **OP quantitation**, a Hewlett-Packard Model 5890 GC with a FPD(P mode) was used. For separations, a 2-3 m X 0.53 mm I.D. deactivated retention gap and a 15 m X 0.53 mm I.D., 1.0 μm film thickness, DB-17 fused-silica open tubular column (J&W Scientific, Fullerton, CA) were used. The injection liner was the direct flash vaporization type. Nitrogen was used as the carrier gas at a flow rate of about 20 ml/min, with column temperature 170°C and detector and injector temperature of 220°C. The GC and recorder sensitivity was adjusted so that about 1.0 ng chlorpyrifos injected produced about 50 % full scale deflection (FSD).

For **OC quantitation**, a Varian Model 3700 GC equipped with a ECD was used. The column was a 30 m X 0.53 mm I.D., 1.5 μm film thickness, DB-1 bonded phase fused-silica open tubular column with a 1 m X 0.53 mm I.D. retention gap of uncoated deactivated fused silica. The injection liner was the direct flash vaporization type containing an inlet sleeve and glass wool (15). Nitrogen was the detector make up gas at a flow rate of about 55 ml/min. Hydrogen was used as the carrier gas at a flow rate of 15 ml/min, with a column temperature of 200°C, a injector temperature of 220°C and detector temperature of 350°C. The GC and recorder sensitivity was adjusted so that 0.1 ng heptachlor epoxide gave about 50 % FSD.

Procedure

Alumina N Cartridge Suitability Test. Each lot of alumina N cartridges must be tested for proper elution of OC pesticides. Prepare a solution of mixed pesticide standard in hexane so that each ml contains approximately 0.15 μg heptachlor epoxide, 0.12 μg aldrin, 0.16 μg dieldrin, 0.16 μg endrin, 0.38 μg p,p'-DDT and 0.90 μg p,p'-methoxychlor. Test each lot of alumina N cartridges as follows: weigh out a 4 g sample of pesticide free butter-fat and dilute to 7.0 ml with hexane and mix well. Refer to Fig. 1 for column/cartridge configuration. Pipet 3.0 ml of the prepared sample onto the Extrelut QE column and take the sample through the extraction and SPE cleanup procedure through "split the solution in half and transfer each half to a 100

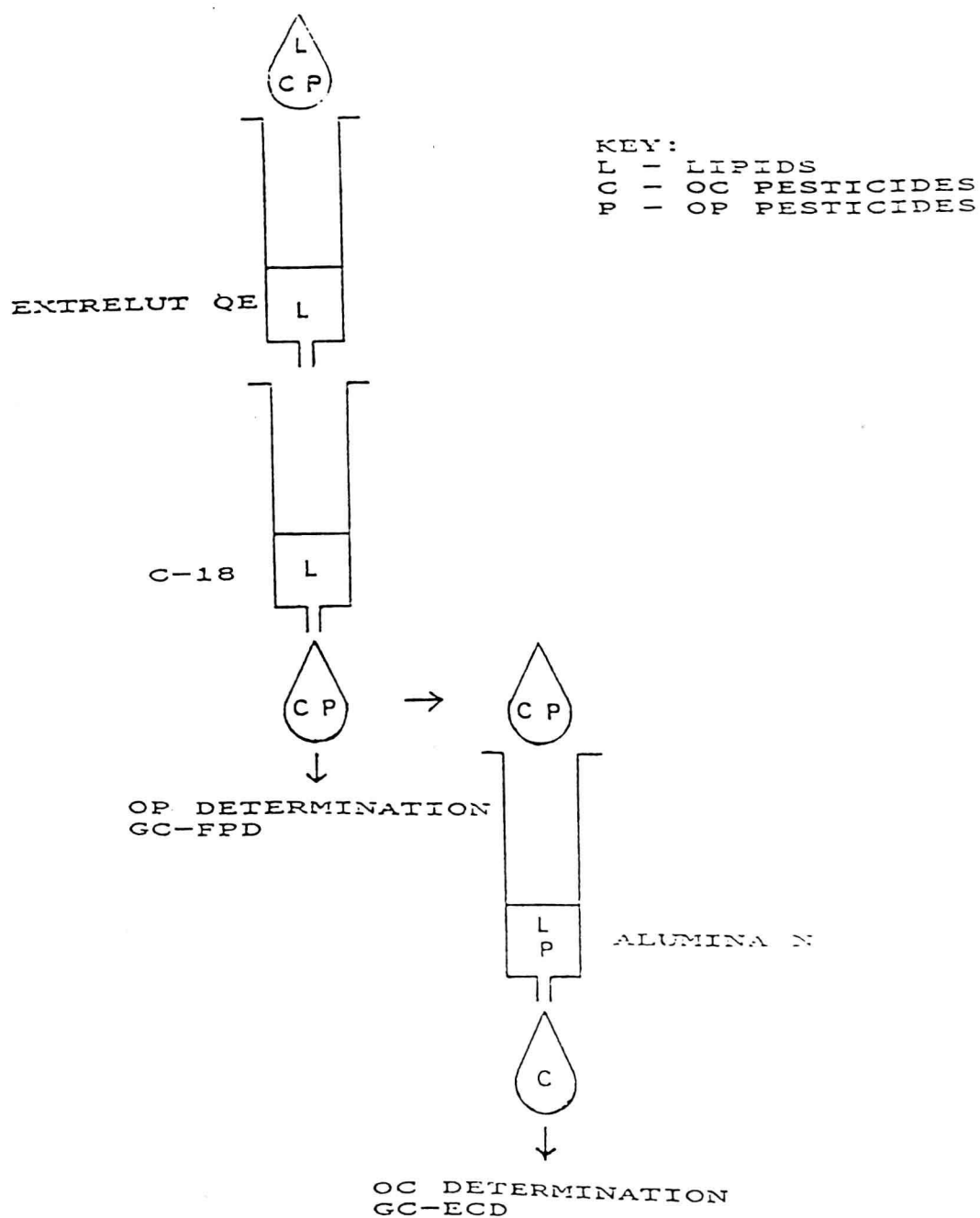


Figure 1. SPE Cartridge Set-Up.

ml evaporating flask". Evaporate both butter-fat blanks to dryness using a vacuum rotary evaporator with a water bath at 50-55° C. Treat both butter-fat blanks to the following procedure: Add 2.0 ml of the mixed pesticide standards to the butter-fat residue and dissolve in 8 ml of 20 % methylene chloride in hexane. Deactivate the 5 g alumina N cartridge by passing 10 ml of acetonitrile containing 0.2 ml of water through the cartridge prior to washing it with 50 ml of 20% methylene chloride in hexane. This prewash is discarded and the standard solution eluted through the alumina N cartridge with an additional 25 ml of 20 % methylene chloride in hexane (total 33 ml) following the steps given in the OC analysis procedure.

Concentrate eluents to 8.0 ml hexane in a glass tube and determine quantitative recovery of each pesticide by injecting into a GC equipped with a ECD using a standard solution in hexane of about the same concentration. Transfer the contents of the glass tube to a weighed fat flask and evaporate to dryness on a water bath at 50-55° C under nitrogen. Dry the flask and determine the lipid carry over. Satisfactory alumina N will permit an average 90 to 105 % recovery of the pesticides and a lipid carry over of 1.5 mg or less.

If the alumina N does not meet this specification a second unused cartridge should be tested by a second method. Follow the preceding directions for testing except omit the deactivation of the alumina with 10 ml acetonitrile containing 0.2 ml of water.

If the lot of alumina N does not meet either of the above specifications, the lot should not be used for OC analysis by this method.

Sample Preparation

Liquify solid fats by warming to about 50° C on a water bath. Separate fat from whole butter by withdrawing a portion of fat for analysis. Mix the oils or fat well and weigh out a 4 g sample into a glass tube. Add hexane to obtain a total volume of 7 ml for a concentration of approximately 0.6 g fat/ml and mix well.

Extraction and SPE Cleanup Procedure

Refer to Figure 1 for column/cartridge configuration. Pipet 3.0 ml (~ 1.8 g) of prepared sample in hexane onto the Extrelut QE column and allow 10 minutes for even distribution of the fat solution. Meanwhile, place the C-18 cartridge on a vacuum system and prewash with about 50 ml

methanol (MEOH) at a flow rate of about 5 ml/min, and discard the washing. Place the Extrelut QE column over the C-18 cartridge and elute both with 20 ml of (1 + 1) methanol/acetonitrile saturated with hexane using light air pressure on the Extrelut QE column to obtain a flow rate of about 3 ml/min (obtain air pressure by connecting a air jet to a vacuum bottle half filled with cotton to catch any particulate material. Attach a hollow rubber tube connected to a hollow glass tube and a #1 rubber stopper to the vacuum bottle. Fit the stopper onto the top of the Extrelut column.) Allow this solution to pass through the C-18 cartridge using gravity flow only and then elute only the C-18 cartridge with 20 ml of methanol using gravity flow. Collect the eluate in a suitable receiver. Transfer the eluate to a 50 ml volumetric flask using acetone. Dilute to volume and mix well. Split the solution in half and transfer each half to a 100 ml evaporating flask. Do not leave in methanol-acetonitrile overnight to prevent low recovery of OP pesticides. Evaporate the OP solution to dryness and the OC solution to about 5 ml using a vacuum rotary evaporator with a water bath at 50-55° C. For the OC analysis, add 20 ml isooctane and evaporate to about 2 to 3 ml using the vacuum rotary evaporator with the water bath set at 60-65 °C. For the **OP analysis** take one of the flasks and reconstitute the residue in acetone and transfer to a suitable glass tube.

GC Quantitation of the OPS

Dilute or evaporate the sample solution to 5.0 ml and inject an appropriate volume of sample solution into the GC and screen for organophosphorus pesticides. Make other dilutions or evaporations as needed. Quantitation should be done both with a matrix standard (6) and a neat standard. The matrix protects the organophosphorus compounds from adsorption and/or decomposition in hot vaporizing injectors ensuring a more complete transfer from injector to column compared to the results observed when standards dissolved in matrix free solvent are used. In the absence of matrix, recoveries in excess of 100% for residue-free extracts spiked with certain organophosphorus pesticides are observed when neat standards are used for calibration (16).

Caution: acetone solutions tend to concentrate rapidly due to solvent evaporation. The volume of both the sample and standard solutions must be closely checked and adjusted to avoid serious quantification errors.

OC Analysis

(For the **OC analysis**, directions are given assuming that the cartridge must be deactivated with 10 ml of acetonitrile containing 0.2 ml of water. If this is not the case, the deactivation step can be omitted.) Dissolve the residue from the other half of the Extrelut/C-18 eluate in 8 ml of 20% dichloromethane in hexane. Place a 5 g Alumina N cartridge or the equivalent on a vacuum manifold. Deactivate by adding 10 ml acetonitrile containing 0.2 ml water. Prewash with 50 ml of 20% dichloromethane in hexane at about one drop per second and discard the washings. Transfer the sample onto the Alumina N cartridge and elute with an additional 25 ml of 20% dichloromethane in hexane using gravity flow. Collect eluate in a suitable receiving flask. Transfer the eluate to a 100 ml evaporating flask using about 10 ml of acetone and evaporate to less than 3 ml but not to dryness using a vacuum rotary evaporator with a water bath temperature of 50-55° C. Transfer to a suitable glass tube with hexane and dilute or evaporate to 4.0 ml and proceed with the **OC quantitation**. Inject an appropriate volume of sample solution and quantitate by area or by peak heights.

In order to correct for small amounts of GC interferences that might be present in the Extrelut QE or other reagents, carry a pesticide free sample of the same type of fat or oil being analyzed through the same analytical steps and subtract any interfering GC peaks from any corresponding pesticide peaks found in the fat or oil being analyzed.

Results and Discussion

The procedure used consists of on-column partitioning on a macroporous Kieselguhr material in place of the usual liquid/liquid partitioning step. The sample is essentially dispersed over a large surface area. A relatively large volume of solvent is passed over an extremely thin film of sample, and as a consequence, pesticides along with a small amount of lipids are extracted efficiently.

Removal of highly polar and nonpolar components of vegetable oils and butter-fat are effected by a combination of SPE cartridges containing reversed phase (C-18) and normal phase (alumina N) packings. The C-18 column strongly retains lipids which typically consists of acids and esters with long hydrocarbon chains while the pesticides, with relatively little alkyl content are readily eluted. Sep Pak cartridges containing 5 g of C-18 packing were tested and found to provide adequate cleanup of lipids for OP pesticide quantitation using the FPD.