

## Committee on Residues and Related Topics

### Pesticides and Other Chemical Contaminants

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#### Summary

##### *Study Director Topics*

*Chlorinated dioxins.*—Topic Advisor Douglas G. Hayward, U.S. Food and Drug Administration, HFS-336, 5100 Paint Branch Pkwy, College Park, MD 20740-3835, Tel: 301-436-1654, Fax: 301-436-2632, E-mail: douglas.hayward@cfsan.fda.gov. Reports further testing for a single automated approach for all food matrixes requiring polychlorinated dibenzo-dioxin/ polychlorinated dibenzofuran, polychlorinated biphenyl, and polybrominated diphenyl ether (PCDD/F, PCB, and PBDE) measurements has been delayed during this year. We are waiting for some new instrumentation to facilitate the automated cleanup procedure. Work has begun on PBDE and pesticide data acquired using a Waters gas chromatograph/time-of-flight (GCT) mass spectrometer and ultra-performance liquid chromatograph/tandem mass spectrometer (UPLC-MS/MS). Methods have been written for PBDEs and 380 pesticides (170 by GCT and 210 by UPLC/MS/MS).

A new J2 Scientific (Columbia, MD) system column using 70% ethyl acetate/cyclohexane appears to remove sulfur from persistent organic pollutants (POPs) samples so that further cleanup may not be necessary and sulfur removal with silver nitrate silica gel can be omitted. The new express gel permeation chromatography (GPC) column is faster than the older 50% dichloromethane (DCM) express column and requires only 22 min for each run with a solvent pump rate of 5 mL/min. (12 min discard, 8 min collect) for PCBs/PBDEs and PCDD/Fs. The same column was tested for 380 pesticides spiked in solvent or in ginseng extracts. The ginseng high molecular weight fraction is mostly removed (>85%) as seen by UV detection and sample color while maintaining good pesticide recoveries (>50–100%). Lower recoveries were observed for some larger pyrethroid-type pesticides such as fluvalinate tau and acrinathrin. Collection was extended in order to collect all of the latest eluting pesticide, pentachlorothioanisole (8 min discard and 8 min collect). The GPC is still the slow step in the cleanup, but now the speed has been double from 1.5 to almost 3 samples/h.

J2 Scientific GPC system allows operation of 3 modules (GPC, dioxin and Accuvap) together. However, the Accuvap evaporation module showed lower recoveries for PCBs than is desired using dichloromethane/ cyclohexane as the mobile phase. It is not clear whether different conditions would work better or not. The flow rate of the GPC is fixed to 5 mL/min so the Accuvap must also evaporate the sample eluting at about 5 mL/min (rapidvap is evaporating an equivalent volume at approximately 2–3 mL/min). Also, noise levels increased with use of the online evaporation. A rapidvap was purchased (Labconco Corp., Kansas City, MO) and this equipment successfully evaporated pesticides, PCBs, and PBDEs with good recoveries in 20–25 min from volumes of either 6 mL × 24 samples for QuEChERS extracts or 45 mL × 8 samples for GPC fractions.

A new procedure for pesticide cleanup in dietary supplements was tested with ginseng that uses accelerated solvent extraction (ASE) with ethyl acetate followed by GPC and tandem solid-phase extraction (SPE) utilizing primary-secondary amine and graphitized carbon sorbents cartridges. Recoveries are currently being evaluated.

##### *Triazines in Raw Agricultural Commodities*

Topic Advisor Robert A. Yokley, Syngenta Crop Protection, Inc., PO Box 18300, Greensboro, NC 27409, Tel: 336-632-2142, Fax: 336-632-7645, E-mail: Robert.yokley@syngenta.com. Reports annual publications on the analysis of triazines in raw agricultural commodities continue to be few. Methods rely primarily on the use of MS for the measurement of final fractions for triazine compounds due to its high degree of sensitivity, selectivity, and confirmatory ability. Methods and one collaborative study are presented for this reporting period on the analysis of one or more of 3 triazines (atrazine, simazine, and/or terbuthylazine) in olive oil, olives, fruits, and vegetables.

The utility of using LC/time-of-flight-MS (LC/TOF-MS) for the analysis of atrazine, simazine, and terbuthylazine in olive oil was reported (1). Olive oil samples were prepared for analysis using a previously reported procedure. In summary, 5 g olive oil were dissolved in 15 mL petroleum ether (saturated with acetonitrile) and subjected to liquid-liquid partitioning with 25 mL acetonitrile (saturated with petroleum ether) followed by a second partitioning step into 10 mL acetonitrile. A 7 mL portion of the pooled acetonitrile fraction was transferred to a 10 mL glass test tube and carefully evaporated to approximately 2 mL. This fraction was homogenized with 2 g aminopropyl-bonded silica (Bondesil-NH<sub>2</sub>, 40 μm particle size) until a fine powder was obtained (matrix solid-phase dispersion). This powder was transferred to a minicolumn containing 2 g Florisil® (12 mL Bond Elute) followed by elution with 2 × 5 mL acetonitrile.

The acetonitrile fraction was evaporated to near dryness, reconstituted in acetonitrile–water (1 + 1), and filtered through a 0.45  $\mu\text{m}$  PTFE filter prior to injection. Analyte identification was accomplished via accurate mass measurement of the protonated  $[\text{M} + \text{H}]^+$  molecule, accurate mass measurement of the main fragment ion, and the characteristic chlorine isotopic abundance profiles. Due to severe signal suppression, matrix-matched standards were required for quantification. Analyte recoveries ranged from 81 to 111% but the concentrations at which these recoveries were obtained were not reported. The limit of detection (LOD) was estimated to be 1 to 1.5  $\mu\text{g}/\text{Kg}$  at a signal-to-noise (S/N) ratio of 3 for these 3 analytes. The S/N ratio was improved, even when using matrix-matched standards, due to the narrow mass windows employed for quantification. Isobaric interferences could be discriminated within 50 milliDaltons.

A sample preparation procedure for the analysis of atrazine and simazine (and 25 other compounds) in fresh and processed olives was described (2). Olive samples of 25 g were extracted in 60 mL acetonitrile for 1 min, 50 g anhydrous sodium sulfate was added, and the extraction continued for another 2 min using a homogenizer at 9500 rpm. After centrifugation at 4000 rpm for 3 min, the extraction vessel was transferred to a freezer for a minimum of 4 h or overnight. Upon removal from the freezer, part of the organic phase was transferred to a small beaker leaving the solids behind (including the frozen oil). A 12 mL (9.43 g) portion of the extract, measured by mass, was transferred to a 100 mL round-bottom flask and evaporated to dryness. The residue was reconstituted in 2 mL acetone for GC/NPD analysis (atrazine and simazine) or 2 mL acetonitrile for GC/ECD analysis. The acetonitrile portion required further cleanup using a 500 mg SepPak alumina-N cartridge prior to GC/ECD analysis. The recoveries for atrazine and simazine were 91 and 92%, respectively, for fresh olives and 90 and 92%, respectively, for processed olives at a limit of quantitation (LOQ) of 0.05 mg/Kg. The RSDs were 8% or less. The application of low-temperature fat precipitation provided an effective means to reduce the amount of oil and fat remaining in the final fractions for analysis. This increased the number of possible injections before the GC column required clipping or replacement and resulted in fewer interfering peaks. The method could be improved by using GC/MSD instead of NP and EC detectors.

A method was described for the analysis of 52 non-easily GC-amenable pesticides (including one easily GC-amenable triazine, atrazine) in fruits and vegetables using LC-ESI/MS/MS (3). The selected commodities for study were chosen based on high water (tomatoes), high acidity (lemons), high sugar (raisins), and high lipid content (avocados). A 20 g homogenized sample was blended at 8000 rpm for 2 min with 60 mL methanol–water (80 + 20) containing 0.1% acetic acid. The extract was then filtered and the solids were washed with the same solvent to obtain a final volume of 100 mL. This extract was diluted 8-fold with LC grade water and a 2.5 mL aliquot portion was removed and diluted further to a volume of 20 mL before taking 5 mL for SPE cleanup using 200 mg Oasis HLB cartridges. The large dilutions were required to

reduce the methanol content so as to avoid breakthrough on the SPE cartridges. The SPE cartridges were preconditioned with 5 mL methanol, 5 mL methanol–MTBE (10 + 90, v/v) 0.1% acetic acid, and finally 5 mL of 1.0% acetic acid. After loading the sample, the cartridge was dried for 1 h before elution with 5 mL methanol–MTBE (10 + 90, v/v) 0.1% acetic acid. Water (0.5 mL) was added to the eluate which was then evaporated until 0.5 mL remained. This fraction was adjusted to 1.0 mL using methanol–MTBE (10 + 90, v/v). The LC conditions (methanol–water in 0.01% acetic acid) were adjusted such that no more than 10 analytes eluted within a 3–4 min time window. This allowed a dwell time of 0.1 s/transition which resulted in satisfactory peak shape. The average recoveries for atrazine in each sample matrix type ranged from 81 to 86% at an LOQ of 0.01 mg/Kg. Due to the high number of monitoring transitions required for 52 compounds, confirmation of an analytes identity required an independent second injection. Matrix-matched standards were required to avoid suppression issues.

The use of hollow fiber supported liquid membranes (HFSLM) was reported for the extraction of 23 compounds (including atrazine, simazine, and terbuthylazine) from cucumber, tomato, and pepper extracts for analysis using LC-ESI/MS (4). Various steps in the procedure were studied to evaluate their effects on extraction efficiency. These include the composition of the organic phase (1% trioctylphosphine oxide in dihexyl ether), pH (4), water and salt content (no water beyond what is in the crop and 15% NaCl), methanol content (20%) of the acceptor solution (100 mM HCl), shaking speed (40/m) and time (1 h), etc. This optimized procedure is summarized as follows: 10 g well-homogenized sample are placed in a 20 mL vial to which is added 1.5 g NaCl and 5 mL buffer at pH 4 (acetic acid–acetate, 0.1 M). A 25 cm length of fiber was filled with acceptor solution and impregnated by soaking in the organic phase for 10 s followed by washing to remove excess organic phase. The fiber was then placed the same vial containing the vegetable extract and shaken at 40 oscillations/m for 1 h. After shaking, the fiber was removed and the acceptor solution was collected by flushing into a 150  $\mu\text{L}$  vial. To this was added 85  $\mu\text{L}$  LC mobile phase and a 20  $\mu\text{L}$  volume was injected into an LC/ESI-MS system for analysis. The results obtained for each analyte were very good when compared to those obtained using a well-established procedure and method for the analysis of these compounds in vegetable matrices. This comparison was required since HFSLM is an equilibrium technique and does not rely on 100% extraction of the analyte. The LOD and LOQ were defined as 3 and 10 $\sigma$  (S/N ratios of 3 and 10) and varied from 0.2 to 1.8 and 0.6 to 6.1  $\mu\text{g}/\text{Kg}$ , respectively, for the 3 triazine compounds. These concentrations are below the MRLs specified by the European Union (EU). Although the analysis of many sample types results in signal suppression or enhancement when using ESI, the final fraction components responsible for these adverse effects were adequately removed using the HFSLM extraction. The repeatability and reproducibility of the measurements were acceptable.

A collaborative study involving 13 laboratories in 7 countries was reported in which 26 compounds (20 fortified and 8 incurred residues), including atrazine, were validated in various fruit and vegetable matrixes (grapes, lettuces, and oranges) using the QuEChERS method (5). In summary, this method involves (1) extraction with acetonitrile (1% acetic acid) in the presence of  $MgSO_4$  and NaOAc, (2) mixing a portion of the extract with  $MgSO_4$ -primary secondary amine for dispersive SPE followed by centrifugation, and (3) analysis of the final fraction by GC/MS and/or LC/MS/MS to cover the wide range of pesticide residue types. The acceptability of the results was based primarily on recovery, intralaboratory repeatability, interlaboratory reproducibility, and the Horwitz ratio. The method met the acceptance criteria standards of AOAC for all analytes. Among the 26 analytes, 21 had HorRat <1.1 and all except one met the LOQ criterion of <10 ng/g. Although not tested here, this multiresidue procedure is applicable to numerous other analytes and is likely applicable to most parent triazines as well.

#### *Pesticides in Foods Using Acetonitrile Extraction and Partitioning with Magnesium Sulfate*

Study Director Steven J. Lehotay, U.S. Department of Agriculture, Agricultural Research Service, Regional Research Center, Food Safety Research Unit, 600 East Mermaid Ln, Wyndmoor, PA 19038, Tel: 215-233-6433, Fax: 215-233-6642, E-mail: Steven.Lehotay@ars.usda.gov. The QuEChERS concept entails extraction with an organic solvent of food samples containing >75% moisture (water is added to dry foods), partitioning with  $MgSO_4$  and/or other salts to separate the extract from water, and using dispersive SPE for cleanup. The original method uses a 10 g sample, 10 mL acetonitrile for extraction by shaking, 4 g  $MgSO_4$  + 1 g NaCl for partitioning followed by centrifugation, and cleanup with primary secondary amine (PSA) sorbent. This approach has been demonstrated in multiple laboratories to give ≈100% recoveries for hundreds of pesticides in many fruit and vegetable matrixes using (GC and LC) with MS for analysis. QuEChERS is very adaptable and flexible, and analysts may use other sample types and sizes, acetone or ethyl acetate extraction solvents, blending instead of shaking, other salt combinations for partitioning, other sorbents in dispersive SPE, or other detectors in GC or LC. A recent overview by R.E. Majors appeared in *LC-GC North America* which describes the QuEChERS approach (6). At least 2 interlaboratory validations were performed using the QuEChERS approach. The AOAC INTERNATIONAL Collaborative Study Protocol of the QuEChERS method incorporated a buffering approach to improve stability and recoveries for a few polar pesticides analyzed by LC/MS. Both GC/MS and LC/MS/MS were used in the analysis. The sample size was increased to 15 g and the amount of extraction solvent and salts were scaled up appropriately. Buffering at pH 4.75 was achieved by adding 1% acetic acid to the acetonitrile and sodium acetate replaced sodium chloride in the partitioning step. The interlaboratory trial of the method was successful among the 13 laboratories in 7 countries for the

27 pesticides evaluated at 10–1000 ng/g concentrations in 3 commodities (lettuce, grape, and orange). The method was approved by AOAC and is now First Action AOAC Official Method **2007.01**.

QuEChERS has also been validated through the European Committee for Standardization (CEN) in an interlaboratory trial conducted in Germany. The study is listed as CEN #00275154 prEN 15662 “Foods of plant origin—Determination of pesticide residues using GC/MS and/or LC/MS(/MS) following acetonitrile extraction/partitioning and cleanup by dispersive SPE-QuEChERS method.” This protocol uses citrate salts for buffering rather than acetate and included graphitized carbon black in the dispersive SPE cleanup step as well as PSA. A Website, [www.quechers.com](http://www.quechers.com), operated by Michelangelo Anastassiades in Germany, provides additional information and results.

Commercial products are available from United Chemical Technologies (Bristol, PA), Supelco (Bellefonte, PA), and Restek (Bellefonte, PA), and perhaps other suppliers, for both official protocols of the QuEChERS method, as well as for the original method and certain modifications preferred by some laboratories. The suppliers will usually provide other amounts of the materials in custom fashion if requested by the customer. Other laboratories are starting to incorporate the dispersive SPE approach in their methods for a variety of applications, such as veterinary drug residue analysis, clinical methods, and acrylamide analysis.

In the past few years, Lehotay and Anastassiades have given numerous presentations and led several QuEChERS training workshops around the world. Several other laboratories have validated and implemented the QuEChERS method for the routine monitoring of pesticide residues. In just a few years since its introduction in a presentation in 2002 and publication in 2003, the QuEChERS approach has become a well-established sample preparation tool for pesticide residue analysis and is growing rapidly in terms of wide usage, number of publications, and expanding applications.

#### *Miniaturized Methods*

Associate Referee Frank Schenck, U.S. Food and Drug Administration, Southeast Regional Laboratory, 60 Eighth St NE, Atlanta, GA 30309, Tel: 404-253-1200, Fax: 404-253-1208, E-mail: [fschenck@ora.fda.gov](mailto:fschenck@ora.fda.gov). Evaluated a variation of the Quechers method developed by Jon Wong at FDACFSAN. This method entails extracting the sample with acetonitrile, salting out with sodium chloride and magnesium sulfate, adding 1 part toluene to 3 parts of acetonitrile extract, and performing the dispersive SPE cleanup with graphitized carbon black (GCB) and PSA. A modified QuEChERS which entails using GCB/PSA columns for the SPE cleanup, with an acetone-toluene elution solvent was also evaluated. In both cases it was found that the presence of toluene either greatly reduced or prevented the degradation of base sensitive pesticides such as chlorothalonil. Since the samples could be extracted with acetonitrile rather than an acetic acid-

acetonitrile mixture, a much better cleanup of the fatty acid matrix coextractants was achieved.

#### *Multiresidue Pesticide Methods by GC/MS and LC/MS*

Topic Advisor Guo-Fang Pang, Qinhuangdao Entry-Exit and Quarantine Bureau, No. 39 Haibin Rd, P.C. 066002, Qinhuangdao, People's Republic of China, Tel/Fax: 86-335-341-7119, E-mail: panggfciq@pang.com.cn. Continues to study residue analysis technology of 800 pesticides and veterinary drugs in foods commonly used in the world with the following achievements: The original 4 pesticide multiresidue methods have been expanded to 8, and GC/MS and LC/MS/MS in the original methods have been separated, either of which has become an independent national standard of the People's Republic of China. The pesticide varieties of 60–70 by LC/MS/MS in the former method have been expanded to 372–405 and the number of pesticide varieties by GC/MS for the 4 methods has also increased to an average of 100. Thus, the total number of pesticide varieties for these 8 pesticide multiresidue methods has reached 655. The study papers for the 4 original national standards have been respectively published in *J. AOAC Int.*, *Anal. Bioanal. Chem.*, *J. Chromatogr. A*, and *Food Addit. Contam.* (7–10). Four papers for these 8 new national standards are currently in the preparation process and under compilation.

#### *Ultra-Trace Method for Pesticides in Bottled Soft Drinks*

Study Director Paul Milne, Pepsi Cola Co., Valhalla, NY 10595, Tel: 914-742-4743, Fax: 914-749-3323, E-mail: pmilne@pepsi.com. Reports that the LC/MS/MS and GC/MS methods have had their single-laboratory validation (SLV) results published in the *J. AOAC Int.* (11, 12). The methods were sent for collaborative study and the experimental work for this has been completed. The data are being evaluated and will be written in report form and then submitted to AOAC via ScholarOne. The LC method was evaluated by 9 laboratories while the GC method was evaluated by 8. At this point, there is no information on method performance.

Both methods were submitted to the Expert Review Panel (ERP) for consideration as methods that can measure residues <1 ng/mL in soft drinks. The ERP included both methods among methods worthy of collaborative study during their meeting in New Delhi, India, in February. An official of the Government of Singapore who works in the Veterinary Public Health Laboratory there has already requested a copy of the SLV that was published. Thus, the interest in this method is beginning to spread and the committee may need to prepare for possible studies dealing with matrix or analyte extensions of the method.

#### *Use of Post-Extraction Gel Permeation Chromatography (GPC) Cleanup for Residue Analysis in Foods: A Summary of Published Articles 2006–2007*

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Tel: 608-828-3226, Fax: 608-831-4451, E-mail: mhalvorson@gilson.com. Reports a number of articles were written this past year that utilized GPC as a post-extraction cleanup method for a variety of seafood products prior to residues analysis. Guo et al. (13) utilized GPC to clean up extracts from seafood products such as shrimp, crab, and shellfish. GPC aided in the removal of interfering lipids prior to analysis for organochlorine pesticides by GC/MS. A GPC column containing 40 g BioBeads™ SX-3 and a mobile phase of dichloromethane–*n*-hexane (1 + 1) was used for extract cleanup. The fraction at 110 to 280 mL was collected, concentrated, and further cleaned using alumina prior to analysis. A total of 212 seafood products from the South China coast were analyzed. DDT isomers were found to be the most predominant contaminant. Morris et al. (14) utilized GPC for the cleanup of fatty fish extracts (cod and trout) prior to analysis for polybrominated diphenyl ethers (PBDEs) and hexabromocyclodecane (HCB) stereoisomers. GPC cleanup was accomplished using 2 cross-linked divinylbenzene gel columns (Polymer Laboratories, Amherst, MA) in series. The mobile phase was either dichloromethane or ethyl acetate–cyclohexane (1 + 1). The determinative method was either GC/MS or GC/ECD for PBDEs and LC-ESI-MS for HCBs. Pulkrabova et al. (15) also utilized GPC cleanup to remove interfering lipids from fish tissue (barbel, bream, chub, perch, and trout) prior to analysis for PBDEs and HCB stereoisomers. Fish were surveyed from the Elbe River. The highest concentrations of these compounds as found in bream fish and the lowest concentrations in perch and trout. Mekebri et al. (16) developed and validated a GC/ECD and GC/MS/MS method for the analysis of synthetic pyrethroids from fish tissue. Accelerated solvent extraction (ASE) was used to extract the pyrethroids from tissue samples followed by GPC cleanup and then a Florisil™ cleanup step. Method detection limits were 0.5 to 5.0 ng/g fresh weight. The International Council for the Exploration of the Sea (ICES) published guidelines recommending GPC cleanup of fish tissue (as well as other marine life) extracts prior to analysis for PBDEs and HBCD stereoisomers (17).

Two studies utilized GPC cleanup to separate lipids in edible oils from pesticides and polyaromatic hydrocarbons (PAHs). Fromberg et al. (18) validated a semi-automatic method for the clean up of vegetable oils (olive, grapeseed, rapeseed, sesame, and sunflower) prior to PAH analysis by GC/MS. The extract cleanup method combined GPC cleanup with SPE cleanup on the same sample preparation system. A number of oils were sampled from Danish markets for the presence of PAHs. Only one sample contained benzo(a)pyrene. Ballesteros et al. (19) developed a multiresidue method for determining pesticides and PAHs from virgin and refined olive oils as well as olive-pomace oil. Samples were extracted using acetonitrile–*n*-hexane followed by GPC cleanup. The determinative method was GC/MS/MS.

GPC post-extraction cleanup was also utilized for the removal of lipids from animal tissue (meat products). Pang et al. (20) validated the use of GPC cleanup prior to analysis of 660 pesticide residues in beef, mutton, pork, chicken, and

rabbit tissue by either GC/MS or LC/MS. A GPC column (425 × 25 mm) packed with Biobeads S-X3™ was used. The mobile phase was ethyl acetate–cyclohexane (1 + 1) at a flow rate of 5 mL/min. Fractions were collected from 22 to 40 min, concentrated and reconstituted in appropriate solvent for analysis. Recoveries from 40 to 120% were reported with LODs ranging from 0.2 to 600 µg/kg. Reinik et al. (21) used GPC to remove lipids from processed meat products prior for 12 PAHs. Hooper and Holden (22) utilized post-extraction GPC cleanup for eggs prior to analysis for 14 PBDE congeners. Determination was by high resolution GC/MS.

Four studies used GPC for the cleanup of extracts from grains, fruits, and vegetables prior to pesticide analysis. Ueno et al. (23) developed a method for the determination of the insect control agents Spinosyn A and D from cabbage, fig, strawberry and the herb, green perilla. A GPC cleanup step was used followed by cleanup using a 2-layered SPE column with graphitized carbon on top and silica gel on the bottom. The GPC mobile phase was acetone–cyclohexane (3 + 7) and final determination was by HPLC-UV/MS. Recovery was >85% with a LOD of 0.001 µg/g by LC/MS. Anand et al. (24) developed an enzyme-linked immunoabsorbent assay (ELISA) method for the detection of the *n*-methylcarbamate insecticide, bendiocarb. Matrix effect studies were performed using a variety of vegetable and cereal samples. Paddy rice required a GPC cleanup step or a C18 column cleanup step in order to achieve effective results for detecting bendiocarb by ELISA. Recovery was 75 to 95%. Shuling et al. (25) described a multiresidue method for the determination of 102 pesticides in leek. The samples were extracted using acetone and dichloromethane and then subject to GPC cleanup followed by an SPE cleanup step. Final determination was by GC/MS/SIM. Recovery was between 70 to 113% with an LOQ of 0.01 mg/kg. The method was also used on other vegetables like capsicum, cucumber, eggplant, and spinach. Liu et al. (26) used on-line GPC-GC/MS to determine 97 pesticides in apple, cabbage, carrot, cucumber, orange, potato, and rice. After GPC cleanup, the sample extract was introduced directly onto the GC column by using a switching valve. Recoveries ranged from 70 to 120%.

GPC cleanup was also used in other food products prior to analysis for contaminants other than pesticides. Kleinhenz et al. (27) reported on the development of extensive cleanup methods to remove essential oils from spices prior to analysis for dioxins, and PCDDs, and polychlorinated biphenyls (PCBs). The goal of their study was to reduce costs, solvent use, time for each analysis, and manpower by automating single cleanup steps for PCDDs and PCBs. After extraction using ASE, GPC cleanup was performed using a GPC column filled with 60 g BioBeads SX-3 (BioRad) and a mobile phase of cyclohexane–ethyl acetate (1 + 1) with a flow rate of 5 mL/min. Several additional cleanup steps were then performed including Florisil, activated silica, and cleanup with activated charcoal. Final determination was by GC-HRMS. The automated system gave recoveries of 71 to 105%. Weller et al. (28) used GPC to isolate the plasticizer epoxidized soybean oil (ESBO) from baby food samples.

After extraction and derivatization to 1,3-dioxolanes, the residue resulting from the derivatization was redissolved in 15 mL ethyl acetate–cyclohexane (1 + 1) and subjected to GPC cleanup. The fraction eluting 70 to 100 mL was collected, evaporated to approximately 2 mL for determination by GC/MS. Recoveries ranged from 75 to 115%. Scientists at Hebei University and the Hebei Entry-Exit Inspection and Quarantine Bureau (29, 30) used GPC to remove lipids and other interferences from chili peppers, chili powder, and chili meats prior to analysis for Sudan dyes I, II, III, and IV as well as several other azo-dyes. Final determination was by LC/MS. Using GPC cleanup was important due to high levels of background noise and frequent cleaning of the ion source when GPC was not used. This method was used on over 1000 samples over an 18 month period. Only 2 chili powder samples were found to contain measurable levels of Sudan dye.

GPC cleanup has also been used to remove interfering lipids from cocoa beans prior to analysis for theobromine and caffeine (31).

An excellent summary of methods for pesticide residues analysis used by different countries around the world was recently published by the Codex Committee on Pesticide Residues (32). Several GPC cleanup methods were referenced in this document.

## Recommendations

(1) **2002.03 Pesticides in Nonfatty Foods Using SFE and GC/MS:** Method Advisor Steven J. Lehotay. Adopted Final Action in 2005 and appears in the 18th Edition of *Official Methods of Analysis*. Discontinue topic.

(2) **2007.01 Pesticides in Foods Using Acetonitrile Extraction and Partitioning with Magnesium Sulfate:** Study Director Steven J. Lehotay. The collaborative study was reviewed and adopted as a First Action Official Method of AOAC INTERNATIONAL. Extensions to this method have been evaluated. Continue topic.

(3) **Ultra-Trace Method for Pesticides in Bottled Soft Drinks:** Study Director Paul Milne. Two collaborative studies have been conducted. Results of these studies are being reviewed. Continue topic.

(4) **Chlorinated Dioxins:** Topic Advisor Douglas Hayward. Recommend topic for Community consideration.

(5) **Determination of Residues of Triazines and Their Chloro-Metabolites in Raw Agricultural Commodities:** Topic Advisor Robert Yokley. Recommend topic for Community consideration.

(6) **Miniaturized Methods:** Topic Advisor Frank Schenck. Recommend topic for Community consideration.

(7) **Multiresidue Methods for Pesticides in Foods by GC/MS and LC/MS/MS:** Topic Advisor Guo-Fang Pang. Recommend topic for Community consideration.

(8) **Use of Post-Extraction Gel Permeation Chromatography (GPC) Cleanup for Residue Analysis in Foods:** Topic Advisor Michael Halvorson. Recommend topic for Community consideration.

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