

## Committee on Residues and Related Topics

### Pesticides and Other Chemical Contaminants

#### DAVID SODERBERG

U.S. Environmental Protection Agency, OPP, HED, RRB3, Rm 821D, 7509C, Ariel Rios Bldg, 1200 Pennsylvania Ave, Washington, DC 20460, Tel: 703-308-4137, Fax: 703-305-5147, E-mail: soderberg.david@epamail.epa.gov

#### Summary

The topic *Dioxins by GC/MS* remains vacant.

#### Background

In previous years, we have emphasized a need to classify sample matrixes into groupings by physical properties or composition in order to help rationalize pesticide method characterization and development. This year at the *Florida Pesticide Residues Workshop*, Chris Pappas of the U.S. Department of Agriculture, Pesticide Data Program (PDP), presented such a systematic classification of food commodities for pesticide analysis. He needed to develop groupings in order to minimize the numbers of commodities needed for method QA/QC samples in the Pesticide Data Program. Under his guidance, PDP has reissued their SOP: *PDP-QC-13, Required Compounds, Marker Pesticides, Process Control Compounds and PDP Commodity Groupings*. In this revision, the following 11 groups of commodities are created: (1) Fruits/Juices/Processed Products; (2) Citrus and High Acid Fruits/Juices; (3) High Sugar Fruits; (4) Cucurbits, Fruiting Vegetables, and Leafy Vegetables; (5) High Starch/Root and Tuber Vegetables; (6) High Sulfur (vegetables); (7) Low Oil Cereal Grains; (8) High Oil Cereal Grains; (9) Animal Tissue/High Protein; (10) Dairy Products; and (11) a Group of Single Commodities such as corn syrup, raisins, and tomato paste. This PDP SOP and its rationale are available at the PDP Website (<http://www.ams.usda.gov/science/pdp/Qc13.pdf>).

As in previous years, a very brief review of publications of pesticide methods for foods follows. In this review, no attempt is made to be comprehensive. In particular, only English language papers are included, most single analyte methods are excluded, and the papers included are primarily those that seemed of most interest to this General Referee. As previously, any decisions about what papers to include, and any opinions expressed, are solely those of the General Referee and should not be taken to relate to the U.S. Environmental Protection Agency in any way.

One new edition of a textbook and 4 monographs of interest to this topic have been published this year. A second

edition of the general textbook on residue analysis techniques, *Trace Environmental Quantitative Analysis* (1), is now available. A collection of analyte-specific methods, *Pesticide Protocols* (2), has also been published. There are 2 new works on extraction techniques. *Modern Extraction Techniques* (3) covers an American Chemical Society symposium on this topic presented in 2004. The second book, *Extraction of Organic Analytes from Food* (4), is an attempt to provide a comprehensive list of every procedure in the literature for extraction of organics from foods. Another useful recent book is *Validation of Thin-Layer Chromatographic Methods for Pesticide Residue Analysis* (5). This book is a comprehensive discussion of the state of the art of thin-layer methods for determining pesticide residues.

Several excellent reviews have appeared. Sherma (6) reviewed recent developments in thin-layer chromatography techniques for pesticides. Hernandez et al. (7) reviewed use of high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) for determination of pesticides. Henry (8) examined supercritical fluid extraction and chromatography and pressured fluid extraction; Ward (9) looked at chiral separations; Raynie (10) discussed modern extraction techniques; and Richardson (11) addressed MS of emerging contaminants in food. Kristenson et al. (12) reviewed matrix solid-phase dispersion (MSPD); Gamiz-Garcia et al. (13) discussed chemiluminescent techniques of pesticide analysis; and Carabias-Martinez et al. (14) considered pressurized liquid extraction of foods. Morozova et al. (15) reviewed immunoassays.

Once again this year, in addition to those methods by our own Study Directors and Topic/Method Advisors, a fair number of valuable gas chromatography/mass spectrometry (GC/MS) and HPLC/MS- or HPLC/MS/MS-based multiresidue methods have been published (16–34). Of course, there were also some single-class methods using GC/MS or LC/MS/MS (35–39). Notably in this latter group is an ultra-low level determination of carbamates in eggs by Schenk et al. (40). Seven single analyte MS-based methods should be included here because they were published in *J. AOAC Int.* (41–48). While on the topic of MS-based analyses, note that Aviv Amirav has published a short paper on “A New Type of GC/MS.” This paper discusses a combination of the supersonic molecular beam interface with other advanced GC/MS features to improve a variety of GC analyses, including the determination of the labile and hence difficult to GC carbamates (49).

Meanwhile, publications also continued to describe methods using more classical GC/detector combinations (50–59). One paper addressed enantiomeric separation of pesticides by HPLC (60). Several other methods used electrochemical sensors or biosensors for pesticide

residues (61–64). There was a scattering of methods using single drop microextraction (65–67), a microchip laminar flow microextraction (68), and 2 papers directly examining stir bar microabsorption (69–70). Two other unusual extractions reported were ultrasonic solvent extraction of honey (71) and a membrane-protected carbon nanotube micro-solid-phase extraction (SPE) system (72). Another paper explored the use of ordinary water to extract environmental samples (73), and one paper addressed the stability of pesticides on SPE disks (74).

Molecularly imprinted polymers have begun to show a good presence for pesticide analyses (75–78). There were also a number of papers addressing analyses for dioxins and polychlorinated biphenyls (PCBs; 79–83) and other organohalides (84); and there was a paper on determination of polybrominated diphenyl ethers (85).

This year, several papers addressed what perhaps can loosely be grouped together as chemometric aspects of pesticide analysis. One paper addressed deconvolution of co-eluting peaks using a multivariate technique (86), and one addressed deconvolution of interfering effects in spectrofluorometric determinations (87). There was an interesting paper on estimating the portion of uncertainty in pesticide analysis that was due to sample processing (88). Another paper addressed determination of a “limit of identification” in GC/full scan MS (89), while yet another compared the use of “external” standards versus the method of standard additions in pesticide analysis (90). Finally, any chemometric part of this review would not be complete without including the paper on HorRat by Horwitz and Albert (91).

## Selected Topics

### *Chlorinated Dioxins*

Topic Advisor Douglas Hayward, U.S. Food and Drug Administration (FDA), reports that a single automated approach for analysis of food matrixes requiring polychlorinated dibenzodioxin and dibenzofuran (PCDD/F), PCB, and polybrominated diphenyl ether (PBDE) measurement is now being tested. ASE 300 100 mL cells are packed with sulfuric acid silica gel 60, and dried food portions are then extracted with petroleum ether. The extracts are concentrated quickly on a turbo-vap and then reconstituted in 5 mL 50 + 50 cyclohexane–dichloromethane mobile phase for processing on an express gel permeation chromatography (GPC) column built by J2 Scientific (Columbia, MO). Initially, in 2005, we tested this approach with our own manually run express GPC column with an inline SPE carbon column made by Alltech (Deerfield, IL; ultra-clean 0.3 g carbon column) for PCDD/F trapping. The results were promising with corn oil, fish oil, butter, fish fillet, and carrots.

We purchased an automated GPC system from J2 Scientific in April 2006 to go with our accelerated solvent extractor. The J2 Scientific system provides for automated operation of an express GPC column (smaller column) with online carbon cleanup for dioxins and collection of both

carbon column toluene elution and the collect fraction passing through the carbon containing the PCBs and PBDEs. Both fractions are concentrated automatically and placed into an autosampler vial in 0.5 mL hexane. No further cleanup is necessary, except, if desired, sulfur removal with silver nitrate silica gel. We also run the dioxin fraction through alumina to improve dioxin chromatography, but we are investigating ways to eliminate that step as well.

PCB and PBDE-containing fractions obtained with this cleanup show uniform good chromatography and low noise. Corn oil fortified in quadruplicate shows excellent recoveries for PBDEs (92–107%) and PCBs somewhat more variable due to sulfur in the tandem MS (70–128%). PCBs and PBDEs were spiked at 1 and 2 ppb levels into 5 g corn oil aliquots. Fish oils were measured again using this system as were fish fillets.

Accelerated solvent extraction (ASE) conditions to determine the lipids in powdered milk have been optimized, and ASE conditions for fat removal prior to express GPC have also been worked out for dairy fat. Up to 99% of the fat is removed for fish and corn oil or milk fat before GPC, with milk fat showing somewhat lower removal (>90%) when petroleum ether is used for extraction.

Currently, we are waiting for software from J2 Scientific that will allow operation of all 3 modules (GPC, dioxin, and Accuvap) together. The software now allows operation of any 2 modules. The new software will allow cleanup and concentration to be done automatically for up to 61 samples at a time. Each sample run is about 40 min, including concentration line washing and sample loading. The autosampler allows the injection of 95–100% of a 5 mL sample volume (extract volume); no sample is wasted, so sample sizes can be smaller. We also plan to test a variation of this system for pesticide cleanup using cyclohexane/ethyl acetate mobile phase for the GPC. This mobile phase will be tested for PCBs and PCDD/Fs as well.

We have begun testing GC/time of flight (TOF) for PCB and PBDE measurements. PBDE sensitivity was found to be greater by 10-fold than that found with single quadrupoles (Agilent 5793 MSD).

### *Determination of Residues of Triazines and Their Chloro-Metabolites in Raw Agricultural Commodities*

Topic Advisor Robert Yokley reports that papers on the analysis of triazines in raw agricultural commodities are few in number between May, 2005 and April, 2006. Methods continue to rely primarily on the use of MS for the measurement of final fractions for triazine compounds due to its high degree of sensitivity, selectivity, confirmatory, and multi-analyte capabilities. However, novel single-analyte immunoassay methods with high sensitivity are also reported. As expected, there is continued effort to reduce sample preparation labor intensity and analysis costs and to increase productivity without compromising quantitative extractability or data quality. Methods are presented for the analysis of certain triazine compounds in tomatoes, potatoes, corn, olives, and olive oil and simazine in fruit juice and milk.

A method for the analysis of atrazine, simazine, and ametryn (among other compounds) in tomatoes using SPE and liquid chromatography/ultraviolet (LC/UV) detection was described (92). In addition, commercially available aminopropyl and C<sub>18</sub> SPE sorbents were compared to laboratory-made aminopropyl and C<sub>18</sub> sorbents for sample preparation. The aminopropyl SPE procedure was as follows: a 7 mL volume of acetone was added to a 5 g subsample of tomato followed by homogenization in a Vortex mixer for 30 s. A 7 mL volume of dichloromethane and 7 mL petroleum ether were added, and the mixture was homogenized for another 30 s. After centrifugation at 8 K rpm for 15 min, the organic layer was decanted and concentrated under nitrogen. The residue was reconstituted in 2 mL dichloromethane and loaded onto a 500 mg aminopropyl SPE cartridge (either the commercially available or laboratory-made cartridges) conditioned previously with 2 mL dichloromethane. The analytes were eluted with 2 × 3 mL portions of dichloromethane–methanol (99 + 1, v/v), concentrated to dryness, and reconstituted to 2 mL methanol for LC/UV analysis.

The C<sub>18</sub> SPE cartridge procedure was as follows: a volume of 20 mL acetone–water (1 + 1, v/v) was added to a 5 g subsample of tomato, mixed for 15 min by sonication, and subjected to centrifugation at 8000 rpm for 15 min. After decantation, 20 mL water was added to the supernatant prior to loading onto a preconditioned C<sub>18</sub> cartridge (5 mL methanol and 5 mL water). The analytes were eluted using 10 mL dichloromethane, the solvent was concentrated to dryness, and the residue was reconstituted in 2 mL methanol for analysis. Overall recoveries were best on the commercially prepared aminopropyl SPE columns and ranged from 81 to 127% for all 3 triazine compounds at the 100, 200, and 1000 ppb concentration levels. The limits of detection (LOD) were reported as 14, 15, and 28 ppb and the limits of quantification (LOQ) were 43, 45, and 86 ppb for atrazine, simazine, and ametryn, respectively. Note, in this study, the LOD and LOQ are statistically calculated parameters, and verification by injecting equivalent standard or conducting recovery experiments at these concentration levels was not performed. The final fractions were analyzed using a Purospher RP-18 5 µm particle size column (125 × 3 mm) and an acetonitrile–0.01% aqueous NH<sub>4</sub>OH (35 + 65, v/v) pH 8.4 mobile phase at 0.7 mL/min, with UV detection at 235 nm.

The use of semicovalent molecularly imprinted polymers (MIP) for the isolation of atrazine, simazine, propazine, and the metabolites deethylatrazine and deisopropylatrazine from potato and corn samples prior to analysis using LC/UV was reported (93). The authors described the preparation and testing of a highly homogeneous binding site distribution MIP with higher capacities and fewer nonspecific binding sites than MIPs prepared using the noncovalent approach. This resulted in final fractions for LC/UV analysis that contained far fewer interfering components and allowed quantification of the analytes at much lower concentration levels. Synthesis of the propazine methacrylate and subsequent polymerization to create the polymer particles was described in detail. The

recoveries ranged from 81 to 97% for the 5 analytes in potato and corn samples at the 20 ppb concentration level. The detection limits at 3 times the signal-to-noise (S/N) ratio ranged from 0.4 to 1.1 ng/g. A Kromasil ODS column, 5 µm particle size (250 × 4.6 mm) with a gradient elution of 80:20 to 20:80 water–acetonitrile in 25 min was used for analysis. Detection was performed using UV at 220 nm.

MSPD was reported for the preparation of olive and olive oil samples for the analysis of atrazine, simazine, terbuthylazine, and 9 other compounds using either GC/MS or LC/MS<sup>n</sup> (ion trap; 94). Representative 1 g samples of olives were blended with 2 g aminopropyl sorbent (Bondesil-NH<sub>2</sub>, 40 µm particle size) until a fine powder was formed. This mixture was transferred to the top of a column already containing 2 g Florisil<sup>®</sup> followed by elution of the 12 analytes with 2 × 5 mL acetonitrile. This fraction was evaporated to dryness and the residue reconstituted in acetonitrile–water (1 + 1) for LC/MS analysis (or acetonitrile only for GC/MS analysis). For olive oil samples, a 5 g portion was dissolved in 15 mL petroleum ether and subjected to liquid–liquid extraction (LLE) with 25 mL acetonitrile (saturated with petroleum ether) and then 10 mL acetonitrile. The 2 acetonitrile phases were pooled, evaporated to a volume of about 2 mL, and blended with 2 g aminopropyl sorbent. The remaining cleanup steps were the same as the olive sample treatment described previously. The detection limits for atrazine, simazine, and terbuthylazine in olive and olive oil samples using LC/MS<sup>n</sup> were 0.8, 1, and 0.4 and 0.5, 1, and 0.2 µg/kg, respectively, based on an S/N ratio of 3 for the lowest concentration of matrix-matched standard injected. The lowest recovery concentration level studied was 10 µg/kg and the recoveries and relative standard deviations (RSD) for olives and olive oil samples ranged from 81 to 103% (RSD ≤ 10%). The recoveries ranged from 99 to 111% (RSD ≤ 8%) for the 100 µg/kg fortified samples. The added selectivity afforded by MS<sup>n</sup> provided detection and quantification at lower concentration levels than that possible using solely GC/MS.

In a companion report to ref. 3, the preparation of olive oil samples using MSPD for the analysis of terbuthylazine by LC-ion trap mass spectrometry (ITMS) or TOF-MS was described (95). An olive oil sample was dissolved in petroleum ether saturated with acetonitrile and subjected to LLE by partitioning twice into acetonitrile saturated with petroleum ether. An aliquot of the pooled acetonitrile extract was homogenized with aminopropyl-bonded sorbent until a fine powder was obtained. This was transferred to the top of a mini-column containing Florisil and terbuthylazine was eluted using acetonitrile. This fraction was concentrated, reconstituted in acetonitrile–water (50 + 50, v/v), and filtered through a PTFE filter prior to analysis. The monitoring transition selected for ITMS was the [M+H]<sup>+</sup> precursor ion *m/z* 230 and product ion *m/z* 174. Structural confirmation was attainable even in a complex sample matrix such as olive oil. The same transition can be monitored when TOF-MS analysis is used, but one can also use accurate mass analysis of both the precursor and product ions for confirmatory purposes.

Recoveries and RSDs of 96 and 6%, respectively, were claimed but the concentration level at which these data were obtained was not reported. Matrix-matched standards were used to generate the calibration plot. The LOD was calculated to be 0.2 and 1.0  $\mu\text{g}/\text{kg}$  using ITMS and TOF-MS, respectively, based on a S/N ratio of 3.

An analytical method was reported for the determination of 32 pesticides (including atrazine, simazine, trietazine, terbuthylazine, and terbutryn) in virgin olive oil using GC/nitrogen-phosphorus detection (NPD), electron-capture detection (ECD), and MS/MS (ion trap; 96). A 2 g sample of virgin olive oil was dissolved in 10 mL *n*-hexane and subjected to LLE 3 times with 10 mL acetonitrile. The pooled extracts were concentrated to dryness prior to reconstitution in 10 mL GPC mobile phase. A 5 mL volume of this fraction was injected into the GPC column and the eluate collected between 15 and 20 min. The eluate was concentrated to dryness and the residue re-dissolved in an appropriate volume (typically 1 mL) of cyclohexane containing the internal standards quintozene for ECD analysis and caffeine for NPD analysis (thermionic detection). Matrix-matched standards were used for calibration purposes. Some recoveries suffered from interferences when NPD or ECD were used but all the recoveries using MS/MS were acceptable: 101% for atrazine, 100% for simazine, 104% for trietazine, 95% for terbuthylazine, and 89% for terbutryn. All RSDs were  $\leq 13\%$ . The LOQ, defined as the lowest spiking level at which each pesticide was consistently quantified with an S/N ratio  $\geq 10$  and a RSD  $\leq 20$ , was 5, 3, 10, 1, and 20  $\mu\text{g}/\text{kg}$  for atrazine, simazine, trietazine, terbuthylazine, and terbutryn, respectively, when MS/MS was used. GC/MS/MS is preferred over GC/NPD or GC/ECD because of its confirmatory capabilities (as long as most qualifier ion selections are free of interferences). In this work, the authors demonstrated that higher residues were detected in olive oil extracted from olives collected off the ground as opposed to olives harvested while still in the trees.

The use of magnetic particle-based immuno-supported liquid membrane assay (m-ISLMA) with chemiluminescence detection was reported for the analysis of simazine in fruit juice and surface water (97). Antibodies were immobilized onto magnetic beads which were inserted into the "acceptor" region of a special device (computer-controlled combination of a cartridge in a metallic holder, peristaltic and syringe pumps, 10-position valve, and a photomultiplier tube). An electromotive force (EMF) was used to trap the beads at the bottom of the acceptor, and in another experiment, a second EMF was alternately applied with the first EMF to continually move the beads around in the acceptor region. Immunoextraction analyte in aqueous solution was continuously pumped through the "donor" channel for 14 min at a flow rate of 100  $\mu\text{L}/\text{min}$  resulting in diffusion of the analyte from the donor over a supported organic liquid membrane (di-*n*-hexyl ether) to the acceptor. The analyte was subsequently captured by the antibody beads in the acceptor. A horseradish peroxidase tracer solution was then pumped into the acceptor to saturate the residual free antibody binding

sites, followed by rinsing to remove excess unbound tracer. A horseradish substrate (containing luminal, etc.) was dispensed into the acceptor to react with the antibody bound tracer, generating the chemiluminescence reaction product, which is eluted from the acceptor and detected via the photomultiplier. Under these conditions, the chemiluminescence signal is indirectly proportional to the analyte concentration, and sensitivity was increased when 2 EMF values were used to keep the beads moving in the acceptor region. Undiluted fruit juice completely obliterated the zero analyte dose level when m-ISLMA was used; thus, sample dilution was performed for subsequent analyses. These results demonstrated that either simazine or a cross-reactant species was present in the sample at the 40 ng/L concentration level. Thus, if a cross-reactant species is present, the lower LOD for this approach might be 40 ng/L, although standards could be assayed in the pg/L concentration range. Overall, this appears to be a cost-effective 1-analyte method for the analysis of simazine.

Micro-immuno-supported liquid membrane assay ( $\mu$ -ISLMA) with chemiluminescence detection was reported for the analysis of simazine in orange juice and milk (98). This work is a continuation of the work reported in the previous paragraph and uses a similar device [computer, cartridge, pumps, valves, photomultiplier tubes (PMT), etc.] for conducting measurements. In this report, a porous polymeric support impregnated with an organic solvent (di-*n*-hexyl ether) is sandwiched between a donor and acceptor polymer plate. The acceptor differs from the donor in that its surface is plated with gold onto which an antibody is immobilized via a self-assembled monolayer (SAM) of a sulfur-containing compound. Two different SAMs and the influence of the SAM chain length on the unspecific binding and assay sensitivity were evaluated and discussed. The procedure was similar to that discussed in the previous paragraph. Sample solution was pumped through the donor for 10 min, wherein analyte diffused into the acceptor region and became trapped. Tracer was dispensed into the acceptor to saturate the residual free antibody binding sites, and horseradish peroxidase substrate was dispensed into the acceptor to react with the antigen-bound horseradish peroxidase to generate the chemiluminescence reaction product. Finally, the product was eluted and transported to the PMT for detection (total analysis time of 20 min). Trace level detection of 0.1 ng/L simazine was shown for the analysis of buffer, but orange juice and milk contained trace levels of simazine or nonspecific matrix component cross-reactants. Simazine detection limits in these sample substrates were not discussed.

#### *Pesticides in Nonfatty Foods Using SFE and GC/MS*

Method Advisor Steve Lehotay reports that AOAC Official Method **2002.03** has been published in the 18th Edition of *Official Methods of Analysis* and has been made Final Action. He has learned that the method is being routinely used in Japan.

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

Study Director Steve Lehotay has submitted a draft of his final report on the collaborative study of QuEChERS (which stands for the quick, easy, cheap, effective, rugged, and safe; pronounced "catchers") approach. He reports that a collaborative study was conducted to determine multiple pesticide residues in fruits and vegetables using a quick, simple, inexpensive, and effective sample preparation method followed by concurrent analysis with GC/MS and LC/MS/MS. Twenty representative pesticides were fortified in 3 matrixes (grapes, lettuces, and oranges) at 3 duplicate levels unknown to the collaborators, ranging from 10 to 1000 ng/g. Additionally, 8 incurred pesticide residues were determined. Thirteen laboratories from 7 countries provided results in the study, and a variety of different instruments were used by collaborators. The QuEChERS procedure simply entails 3 main steps: (1) a 15 g homogenized sample is weighed into a 50 mL centrifuge tube to which 15 mL acetonitrile containing 1% acetic acid is added along with 6 g MgSO<sub>4</sub> and 1.5 g sodium acetate (plus an internal standard), and the tube is shaken and centrifuged; (2) a portion of the extract is added to 3 + 1 (w/w) MgSO<sub>4</sub>-primary secondary amine sorbent (200 mg/mL extract), mixed, and centrifuged; and (3) the final extract is transferred to autosampler vials for analysis by GC/MS and LC/MS/MS to determine and identify a wide range of pesticide residues. To achieve <10 ng/g detection limits in modern GC/MS, large volume injection (LVI) of 8 µL is typically needed, or the final extract can be concentrated and solvent exchanged to toluene (4 g/mL), in which case 2 µL splitless injection is used. In the study, the averaged results for data from 7 to 13 laboratories (not using internal standardization) for the 18 blind duplicates at the 9 spiking levels in the 3 matrixes were as follows: atrazine -92 %recovery (18 %RSD reproducibility); azoxystrobin -93 (15); bifenthrin -90 (16); carbaryl -96 (20); chlorothalonil -70 (34); chlorpyrifos -89 (25); cyprodinil -89 (19); *o,p'*-DDD -89 (18); dichlorvos -82 (21); endosulfan sulfate -80 (27); imazalil -77 (33); imidacloprid -96 (16); linuron -89 (19); methamidophos -87 (17); methomyl -96 (17); procymidone -91 (20); pymetrozine -69 (19); tebuconazole -89 (15); tolyfluanid (in grapes and oranges) -68 (33); and trifluralin -85 (20). For incurred pesticides, kresoxim-methyl (9.2 ± 3.2 ng/g) and cyprodinil (112 ± 18) were found in the grapes; permethrins (112 ± 41), cyhalothrin (cyhalothrin (58 ± 11), and imidacloprid (12 ± 2) were determined in the lettuces; and ethion (198 ± 36), thiabendazole (53 ± 8), and imazalil (13 ± 4) were determined in the oranges. Chlorpyrifos-methyl (200 ng/g) was used as a quality control standard added during sample homogenization, and yielded 86% recovery and 19% RSD reproducibility. Intralaboratory repeatabilities for the method averaged 9.8% RSD for all analytes. The collaborative study results demonstrate that the QuEChERS method is fit-for-purpose to monitor many pesticide residues in fruits and vegetables, and the Study Director recommends that it be adopted Official First Action.

### *Miniaturized Methods*

Topic Advisor Frank Schenck, FDA, Atlanta, GA, studied the effect of the solvents used during SPE cleanup on the stability of base-sensitive organochlorine pesticides. The weak anion exchange SPE sorbent, aminopropyl and primary secondary amine (PSA), result in an excellent cleanup for the multiresidue determination of pesticides in fruits and vegetables. Unfortunately, certain base-sensitive organochlorine pesticides will be degraded by these weakly basic SPE sorbents. One approach to preventing this degradation is found in the latest version of the QuEChERS method, which entails extracting with a 1% acetic acid-acetonitrile mix and salting out with sodium acetate and magnesium sulfate. The buffered acidic extract is then subjected to dispersive SPE cleanup using PSA. Although this will prevent the breakdown of the base-sensitive pesticides, it will also result in a less efficient cleanup. Using toluene during the PSA cleanup, without using acid, also helps prevent degradation of base-sensitive pesticides. Romaine lettuce samples were spiked with chlorothalonil, chlorpyrifos, dichlofluanid, captan, captafol, and dicofol. Samples were extracted using the Luke method (acetone extraction, liquid-liquid partition cleanup) and subjected to cleanup on a PSA SPE column, using an acetone-toluene (3 + 1) mixture as the elution solvent. Samples were also extracted using the original version of the QuEChERS method, in which no acetic acid was used, and sodium chloride rather than sodium acetate was used during the saltout. Toluene was added to the acetonitrile extract (1 part toluene to 3 parts acetonitrile) before the PSA dispersive SPE cleanup. When toluene was used during the SPE cleanups, there was very little degradation of the pesticides. When the SPE cleanups were performed without toluene, only chlorpyrifos was not affected; all the other pesticides were rapidly degraded.

### *Synthetic Pyrethroids*

Method Advisor Guo Fang Pang advises that Official Method **998.01** was made Final Action and has been published in the 18th Edition of the *Official Methods of Analysis*.

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

Topic Advisor Guo Fang Pang advises that he is currently organizing the study of 35 national standards for 100 veterinary drug residues. At this time he cannot continue work toward a collaborative study of any of the 4 pesticide multiresidue methods he has submitted. He reports, however, that he is still profoundly attached to doing a collaborative study. Upon completion of the current veterinary drug assignment this year, he expects to renew his efforts to undertake an AOAC Official Method collaborative study.

Regarding the 4 submitted multiresidue methods, the fruits and vegetable method was published in *J. AOAC Int.* (99); the grain and cereal method was published in *Anal. Bioanal.*

*Chem.* (100); the animal tissue method appears in *J. Chromatogr. A* (101); and the honey, fruit juices, and fruit wine method is in *Food Addit. Contam.* (102).

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

Study Director Paul Milne reports that the original method is now 2 methods: an LC/MS method and a GC/MS method. The sample preparation was so much different for each technique that the team decided that it would be more logical to have 2 methods that focused on 2 different sets of residues. The LC method will be used for detecting Alachlor, Atrazine, Butachlor, Isoproturon, Malaoxon, Monocrotophos, Methyl Paraoxon, Phorate, Phorate Sulfone, Phorate Sulfoxide. The GC method will be used for detecting DDT, DDE, DDD, Lindane, Alpha, Beta, and Gamma-HCH, Alpha, Beta-Endosulfan, Endosulfan Sulfate, Ethion, Chlorpyrifos, 2,4-D, Aldrin and Dieldrin.

The single laboratory validation (SLV) for LC is being performed on a Sciex API 4000 and the method has an LOQ of 0.10 ppb for all analytes in the following matrixes: 7-Up (lemon/lime beverage), Diet Pepsi (non-nutritive sweetener beverage), and Lemon/Lime Gatorade (cloudy isotonic, noncarbonated beverage). The GC/MS method is currently ending SLV and can quantitate all analytes in the above 3 matrixes reliably to 50.0 ppb. Some analytes have a lower LOQ, depending upon the matrix, but it will take too much time to determine the LOQ of each analyte in each matrix. Depending upon how quickly the SLV reports go through AOAC INTERNATIONAL, it is hoped to begin multilaboratory validation in late August or early September.

In anticipation of the collaborative study, 2 cans of a cloudy orange beverage (the worst beverage matrix) were spiked tested. This beverage has high sugar, high gum, and high flavor oil content, yet the laboratory was able to observe the analytes of interest rather well. This is one of the matrixes that will be used in the multilaboratory validation.

#### *Post-Extraction GPC Cleanup for Pesticide Residues*

Topic Advisor Michael Halvorson reports on this topic.

*Published articles.*—The use of GPC for post-extraction cleanup of fatty foods before pesticide and herbicide analysis was the primary focus for articles written in the past year. Moreno et al. (103) compared GPC cleanup to SPE cleanup for the removal of lipids from fatty vegetables such as avocado prior to GC/MS/MS analysis for 65 pesticide residues. The authors found that GPC cleanup was more effective than SPE cleanup. Recoveries were 70 to 110% with LODs that were lower than the European Union maximum residue level. Pang et al. (101) validated the use of GPC cleanup before 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. Patel et al. (104) used GPC cleanup to remove lipids from fish oil, pork fat, olive oil, and vegetable oil before analysis for 19 chlorinated pesticides by GC/MS and GC/MS/MS. Montemurro et al. (105) used GPC to separate citrus waxes and oils from the pesticide fenitrothion in oranges and clementines and their leaves. They used a mobile phase of ethyl acetate–cyclohexane (1 + 1) at 5 mL/min. Analysis was by GC/NPD. Murray et al. (106) evaluated AOAC Method 984.21 for the cleanup of beef fat containing both chlorinated pesticides and PBDEs. Some co-elution between PBDEs and chlorinated pesticides (80–90% resolution) occurred when this particular GPC cleanup method was used. Hancock et al. (107) reported on the determination of organochlorine pesticides, synthetic pyrethroids, and PCBs in animal fat. Fat samples were dissolved in ethyl acetate–cyclohexane (1 + 1), spiked at 0.00625 or 0.05 mg/kg, and then subjected to GPC cleanup with the same solvent as the mobile phase. Analysis was by GC/MS/MS. Walker et al. (108) used GPC cleanup before GC/MS analysis for methoprene in lobster tissue.

Two studies used GPC to separate lipids in olive oil from pesticide residues. Guardia-Rubio et al. (96) surveyed olive oil samples from mills in Spain for the presence of 32 organochlorine, organophosphorus, and organonitrogen pesticides. Samples were extracted with acetonitrile saturated in *n*-hexane, concentrated, and then subject to GPC cleanup using a mobile phase of ethyl acetate–cyclohexane (1 + 1). Analysis was by GC/thermionic specific detection, GC/ECD, or GC/MS/MS. Terbutylazine, diuron, and endosulfan sulfate were the most commonly reported pesticides found in olive oil. Mendez et al. (109) evaluated the effects of refining and bleaching to remove pesticides from olive oil. Olive oil was spiked with endosulfan, simazine, oxifluorfon, and diflufenicon. The spiked oil was then subjected to refining, bleaching, or no treatment. After extraction, the extract was subjected to GPC cleanup using a Waters Envirogel guard column (19 × 150 mm) and GPC column (19 × 300 mm). The mobile phase was 100% dichloromethane at a flow rate of 5 mL/min. Collection occurred at 12–22 min. Final analysis was by ion trap MS. Both refining and bleaching were required to remove endosulfan and endosulfan sulfate.

Five studies used GPC cleanup of grains, fruits, and vegetables before pesticide analysis. Zhang et al. (110) used GPC cleanup to determine 109 pesticides in unpolished rice. Rice was extracted with ethyl acetate. The extract was then subjected to GPC cleanup using a column containing Biobeads S-X3 and a mobile phase of dichloromethane–cyclohexane (1 + 1). The flow rate was 5 mL/min. The first 65 mL was discarded to waste. Eluant was collected from 66 to 150 mL. This was then concentrated to 1 mL and further cleaned up using a Florisil column. Analysis was by GC/MS in selected ion monitoring mode. Pesticide residue recovery was excellent with the exception of bifenthrin which elutes earliest off the GPC column. LOD levels were 1–120 ng/g. Ambrus et al. (111) evaluated

thin-layer chromatography (TLC) as a screening method for pesticide residues in fruits, vegetables, and grains. Sample extracts were cleaned with GPC, active carbon, magnesia, or diatomaceous earth before analysis by TLC. Porzano and Cadoppi (112) reported on the use of large volume splitless injections on the GC system to increase the sensitivity for the analysis of pesticides in foods. GPC cleanup was used before analysis of 14 pesticides in beets, strawberries, tomato, and pineapple. No specific details on GPC cleanup procedures were provided. Halvorson et al. (113) reported on the use of GPC cleanup before analysis for fipronil and its major degradation products. Analysis was by GC with halogen-specific detection (XSD). Haixia et al. (114) used online GPC-GC/MS to determine 97 pesticides in carrot, apple, and rice. GPC cleanup was achieved by injecting 10  $\mu$ L extract into a Shodex CLNPak EV-200 column with a flow rate of 0.1 mL/min and a mobile phase of acetone-cyclohexane (3 + 7). After GPC cleanup, the extract was introduced directly onto the GC system by use of a switching valve. Recoveries ranged from 26.22 (captan in rice) to 224.86% (acramithrin in carrot).

GPC cleanup was also used to clean up foods before the analysis of residues and contaminants other than pesticides and herbicides. Attalah et al. (115) used GPC to clean up spice extracts before analysis for aflatoxins B1, B2, G1, and G2. GPC cleanup with HPLC fluorescence detection resulted in LOQs below the current EU regulation limitations. Recovery of aflatoxins was 80–120%. Janska et al. (116) investigated the use of 3 different types of GPC columns and 2 different mobile phases for the cleanup of fish tissue before analysis for 15 polyaromatic hydrocarbons. Halvorson et al. (117) demonstrated the utility of using GPC cleanup before analysis for Sudan dyes as well as other types of dyes that may contaminate spices such as red pepper. Hatano (118) used GPC and HPLC to isolate and characterize several proteinase inhibitors in dried figs. Stark et al. (119) used solvent extraction, GPC, and HPLC to isolate and characterize the key compounds that give cocoa a bitter taste, including glycopyranosides, amino acid amides, and flavan-3-ols.

GPC cleanup has also been used to evaluate genotoxicants in recycled food packaging products. Ozaki et al. (120) evaluated 5 virgin paper products and 7 recycled paper products purchased from supermarkets around Japan. The paper products were cut into 1  $\times$  1 cm squares, weighed to obtain 10 g, and subjected to several LLE steps followed by cleanup through a 6 mL EnviCarb (500 mg) column. The extract was then concentrated and reconstituted in 1 mL tetrahydrofuran (THF). The extract was subject to GPC using a Shodex KF-G and KF-801 column in combination with THF as the mobile phase. Fractions were collected every 30 s. Test fractions were subject to the *rec* assay for genotoxicity and GC/MS to identify the genotoxic compounds. Dihydroabiatic acid and abiatic acid were detected in all 7 recycled paper products.

*Industry news.*—LCTech (Dorfen, Germany) introduced the GPC ULTRA Sample Preparation System and Automated Concentrator in 2005. This system offers fully automated

sample preparation for the modified DFG S19 method, the EN 12393 (pesticides in nonfatty foods) methods, EN 1528 (pesticides and PCBs in fatty foods), and AOAC Method 984.21. The system has the capability of performing the GPC cleanup step followed by sample concentration of the GPC eluent and transfer of the aliquot to a GC or LC vial for further analysis. The system is fully automated and can process up to 52 samples overnight.

J2 Scientific introduced the AccuVap™ In-line concentration system at Pittcon 2006. This system is for use with the J2 AccuPrep MPST™ GPC cleanup system. It allows for the fast and accurate concentration of GPC collect fractions as they elute off the GPC column. The system can perform a solvent exchange before transfer of the extract to a GC system or storage vial before analysis. Data for the use of the system for USEPA 3640A were presented at Pittcon. Studies are currently under way to evaluate the system for EU method EN 1528 and modified DFG S19.

Shimadzu introduced a combination GPC-GC/MS system this year. This system is available only in China to date. Details are described in the section above (Haixia et al., 2006). Sample injection volumes, GPC column sizes and flow rates are limited with this system, so achieving low detection limits may be an issue. Pesticide residue recovery rates also varied widely with this system. More data will be provided at the Dalian International Chromatography Symposium in June, 2007. Shimadzu also introduced a GPC cleanup system on its website in July 2006. No details were provided.

OI Analytical (College Station, TX) introduced a new autosampler (1096TB) for its GPC cleanup system in 2005. This system offers a higher collection vessel capacity and septum piercing to reduce sample evaporation loss and is more robust than its earlier model. A solvent switching option was also added. Gilson, Inc. (Middleton, WI) began offering customized GPC/SPE cleanup systems in limited market areas in 2005–2006.

## Recommendations

(1) *Chlorinated Dioxins.*—Topic Advisor Douglas 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. Continue topic.

(2) *Determination of Residues of Triazines and Their Chloro-Metabolites in Raw Agricultural Commodities.*—Topic Advisor Robert 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. Continue topic.

(3) *2002.03 Pesticides in Nonfatty Foods Using SFE and GC/MS.*—Method Advisor 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: slehotay@errc.ars.usda.gov. Continue topic.

(4) *Pesticides in Foods Using Acetonitrile Extraction and Partitioning with Magnesium Sulfate*.—Study Director Steven J. Lehotay. This very active topic continues to be highly productive and the method is coming into use in several laboratories. Continue topic.

(5) *Miniaturized Methods*.—Topic Advisor 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. Continue topic.

(6) **998.01** *Synthetic Pyrethroids*.—Method Advisor Guo-Fang Pang, Qinhuangdao Entry-Exit and Quarantine Bureau, No. 39 Haibin Rd, P.C. 066002, Qinhuandao, People's Republic of China, Tel/Fax: 86-335-341-7119, E-mail: panggfcq@pang.com.cn. Adopted as Final Action with comments May 2003. This method has been made Final Action and has been published in the 18th Edition of OMA. Discontinue topic.

(7) *Multiresidue Methods for Pesticides in Foods by GC/MS and LC/MS/MS*.—Topic Advisor Guo-Fang Pang. This Topic Advisor has proposed a collaborative study. He is temporarily distracted by other studies, but intends to return to doing a collaborative study when time avails if the Community supports that study. Continue topic.

(8) *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. Methods have been developed, SLVs have been completed, and reports submitted. Continue topic.

(9) *Post-Extraction GPC Cleanup for Pesticide Residues*.—Topic Advisor Michael Halvorson, Gilson, Inc., 3000 Parmenter St, PO Box 620027, Middleton, WI 53562-0027, Tel: 608-828-3226, Fax: 608-831-4451, E-mail: mhalvorson@gilson.com. Continue topic.

## References

- (1) Loconto, P. (2006) *Trace Environmental Quantitative Analysis*, 2nd Ed., CRC Press, Boca Raton, FL
- (2) Vidal, J.M., & Frenich, A.B. (2006) *Pesticide Protocols*, Humana Press, Clifton, NJ
- (3) Turner, C. (2006) *Modern Extraction Techniques: Food and Agricultural Samples*, ACS Symposium, American Chemical Society Press, Washington, DC
- (4) Self, R. (2005) *Extraction of Organic Analytes from Food*, Springer-Verlag, New York, NY
- (5) International Atomic Energy Agency (2005) *Validation of Thin-Layer Chromatographic Methods for Pesticide Residue Analysis*, IAEA-TECDOC-1462
- (6) Sherma, J. (2005) *Acta Chromatogr.* **15**, 5–30
- (7) Hernandez, F., Pozo, O., Sancho, J., Lopez, F., Marion, J., & Ibanez, M. (2005) *Trends Anal. Chem.* **24**, 596–612
- (8) Henry, M. (2006) *Anal. Chem.* **78**, 3909–3916
- (9) Ward, T. (2006) *Anal. Chem.* **78**, 3947–3956
- (10) Raynie, D. (2006) *Anal. Chem.* **78**, 3997–4004
- (11) Richardson, S. (2006) *Anal. Chem.* **78**, 4021–4046
- (12) Kristenson, E.M., Ramos, L., & Brinkman, U. (2006) *Trends Anal. Chem.* **25**, 96–111
- (13) Gamiz-Garcia, L., Garcia-Campana, A., Soto-Chinchilla, J., Huerta-Perez, J., & Gonzalez-Casado, A. (2005) *Trends Anal. Chem.* **24**, 927–941
- (14) Carabias-Martinez, R., Rodriguez-Gonzalo, E., Revilla-Ruiz, P., & Hernandez-Mendez, J. (2005) *J. Chromatogr. A* **1089**, 1–17
- (15) Morozova, V., Levashova, A., & Eremin, S. (2005) *J. Anal. Chem.* **60**, 202–217
- (16) Kakimoto, Y., Naetoko, Y., Iwasaki, Y., Nakamura, S., & Tatsuguchi, H. (2005) *J. Food Hyg. Soc. Jpn.* **46**, 153–160
- (17) Alberio, B., Sanchez-Brunete, C., & Tadeo, J.L. (2005) *Talanta* **66**, 917–924
- (18) Gonzalez-Rodriguez, M., Liebana, F., & Frenich, A. (2005) *Anal. Bioanal. Chem.* **382**, 164–172
- (19) Leandro, C., Fussell, R., & Keely, B. (2005) *J. Chromatogr. A* **1085**, 207–212
- (20) Bogianni, S., Curini, R., Di Corcia, A., Lagana, A., Stabile, A., & Sturchio, E. (2006) *J. Chromatogr. A* **1102**, 1–10
- (21) Tong, L., Ma, X.D., & Li, C.J. (2006) *Anal. Lett.* **39**, 985–996
- (22) Hernandez, F., Pozo, O.J., Sancho, S.V., Bijlsma, L., Barreda, A., & Pittarch, E. (2006) *J. Chromatogr. A* **1109**, 242–252
- (23) Garrido-Frenich, A., Martinez-Vidal, J., Cruz-Sicilia, A., Gonzalez-Rodriguez, M., & Plaza-Bolanos, P. (2006) *Anal. Chim. Acta* **558**, 42–52
- (24) Hercegova, A., Domotorova, M., Matisova, E., Kirchner, M., Otrkal, R., & Stefuca, V. (2005) *J. Chromatogr. A* **1084**, 46–53
- (25) Blasco, C., Font, G., & Pico, Y. (2005) *J. Chromatogr. A* **1098**, 37–43
- (26) Liu, M., Hashi, Y., Song, Y., & Lin, J.M. (2005) *J. Chromatogr. A* **1097**, 183–187
- (27) Rubio, M., Medina, A., Diaz, A., & de Cordova, M. (2006) *J. Sep. Sci.* **29**, 1578–1586
- (28) Garcia-Reyes, J., Ferrer, C., Thurman, M., Fernandez-Alba, A., & Ferrer, I. (2006) *J. Agric. Food Chem.* **54**, 6493–6500
- (29) Kirchner, M., Matisova, E., Otrkal, R., Hercegova, A., & de Zeeuw, J. (2005) *J. Chromatogr. A* **1084**, 63–70
- (30) Tahboub, Y., Zaater, M., & Barri, T. (2006) *Anal. Chim. Acta* **558**, 62–68
- (31) Soler, C., Manes, J., & Pico, Y. (2005) *J. Chromatogr. A* **1088**, 224–233
- (32) Wang, J., Cheung, W., & Grant, D. (2005) *J. Agric. Food Chem.* **53**, 528–537
- (33) Wang, J., & Cheung, W. (2006) *J. AOAC Int.* **89**, 214–224
- (34) Vidal, J., Frenich, A., Lopez, T., Salvador, I., el Hassani, L., & Benajiba, M. (2005) *Chromatographia* **61**, 127–131
- (35) Goto, T., Ito, Y., Yamada, S., Matsumoto, H., Oka, H., & Nagase, H. (2006) *Anal. Chim. Acta* **555**, 225–232
- (36) Esteve-Turrillas, F., Pastor, A., & de la Guardia, M. (2005) *Anal. Chim. Acta* **553**, 50–57
- (37) Thurman, E., Ferrer, I., Zweigenbaum, J., Garcia-Reyes, J., Woodman, M., & Fernandez-Alba, A. (2005) *J. Chromatogr. A* **1082**, 71–80
- (38) Sheridan, R., & Desjardins, L. (2006) *J. AOAC Int.* **89**, 1088–1094
- (39) Shoemaker, J., & Bassett, M. (2006) *J. AOAC Int.* **89**, 201–209
- (40) Schenk, F., Podhorniak, L.J., Casanova, J., & Donoghue, D. (2006) *J. AOAC Int.* **89**, 196–200

- (41) Zimmer, D., Philipowski, C., Posner, B., Gnielka, A., Durr, E., & Dorff, M. (2006) *J. AOAC Int.* **89**, 786–796
- (42) Ginn, R., Wilson, L., de Sousa, S., & de la Calle, M. (2006) *J. AOAC Int.* **89**, 728–734
- (43) Alder, L., & Startin, J. (2006) *J. AOAC Int.* **88**, 1762–1776
- (44) LePage, J., Hebert, V., Tomaszewska, E., Rothlein, J., & McCauley, L. (2006) *J. AOAC Int.* **88**, 1788–1792
- (45) Sannino, A., & Bandini, M. (2006) *J. AOAC Int.* **88**, 1822–1826
- (46) Tsiropoulos, N., Likas, D., & Karpouzias, D. (2006) *J. AOAC Int.* **88**, 1827–1833
- (47) Tsiropoulos, N., Liapis, K., Likas, D., & Miliadis, G. (2006) *J. AOAC Int.* **88**, 1834–1839
- (48) Barreda, M., Lopes, F., Villajoya, M., Beltran, J., Garcia-Baudin, J., & Hernandez, F. (2006) *J. AOAC Int.* **89**, 1080–1087
- (49) Fialkov, A., Steiner, U., Jones, L., & Amirav, A. (2006) *Int. J. Mass Spectrom.* **251**, 47–58
- (50) Yague, C., Bayarri, S., Conchello, P., Lazaro, R., Perez-Arquillue, C., Herrera, A., & Arino, A. (2006) *J. Agric. Food Chem.* **53**, 5105–5109
- (51) Campillo, N., Penalver, R., Aguinaga, N., & Hernandez-Cordoba, M. (2006) *Anal. Chim. Acta* **562**, 9–15
- (52) Rosales-Conrado, N., Leon-Gonzalez, M., Perez-Arribas, L., & Polo-Diez, L. (2005) *J. Chromatogr. A* **1081**, 114–121
- (53) Cardeal, Z., & Paes, C. (2006) *J. Environ. Sci. Health B* **41**, 369–375
- (54) Tang, F., Yue, Y., Hua, R., & Cao, H. (2006) *J. AOAC Int.* **89**, 498–502
- (55) Yi, X., Hua, Q., & Lu, Y. (2006) *J. AOAC Int.* **89**, 225–231
- (56) Herrera, A., Perez-Arquillue, C., Conchello, P., Bayarri, S., Lazaro, R., Yague, C., & Arino, A. (2005) *Anal. Bioanal. Chem.* **381**, 695–701
- (57) Vigna, C., Morais, L., Collins, C., & Jardim, I. (2006) *J. Chromatogr. A* **1114**, 211–215
- (58) Garcia de Llasera, M., Gomez-Almaraz, L., Veera-Avila, L., & Pena-Alvarez, A. (2005) *J. Chromatogr. A* **1093**, 139–146
- (59) Liu, W., Hu, Y., Zhao, J., Xu, Y., & Guan, Y. (2005) *J. Chromatogr. A* **1095**, 1–7
- (60) Wang, P., Jiang, S., Liu, D., Zhang, H., & Zhou, Z. (2006) *J. Agric. Food Chem.* **54**, 1577–1583
- (61) De Souza, D., & Machado, S. (2006) *Electroanalysis* **18**, 862–872
- (62) Yang, Y., Guo, M., Yang, M., Wang, Z., & Shen, G. (2005) *Int. J. Environ. Anal. Chem.* **85**, 163–175
- (63) Manisankar, P., Selvanathan, G., & Vedhi, C. (2005) *Int. J. Environ. Anal. Chem.* **85**, 409–422
- (64) Manisakar, P., Selvanatyan, G., & Vedhi, C. (2006) *Talanta* **68**, 686–692
- (65) Lopez-Blanco, C., Gomez-Alvarez, S., Rey-Garrote, M., Cancho-Grande, B., Simal-Gandara, J. (2006) *Anal. Bioanal. Chem.* **384**, 1002–1006
- (66) Zhao, E., Han, L., Jiang, S., Wang, Q., & Zhou, Z. (2006) *J. Chromatogr. A* **1114**, 269–273
- (67) Yangcheng, L., Quan, L., Guuangsheng, L., & Youyuan, D. (2006) *Anal. Chim. Acta* **566**, 259–264
- (68) Smirnova, A., Mawatari, K., Hibara, A., Prokurnin, M., & Kitamori, T. (2006) *Anal. Chim. Acta* **558**, 69–74
- (69) Bicchi, C., Cordero, C., Liberto, E., Rubiolo, P., Sgorbini, B., David, F., & Sandra, P. (2005) *J. Chromatogr. A* **1094**, 9–16
- (70) Zuin, V., Schellin, M., Montero, L., Yariwake, J., Augusto, F., & Popp, P. (2006) *J. Chromatogr. A* **1114**, 180–187
- (71) Rezic, I., Horvat, A., Babic, S., & Kastelan-Macan, M. (2005) *Ultrason., Sonochem.* **12**, 477–481
- (72) Basheer, C., Ainedhary, A., Rao, B., & Valliyaveetil, S. (2006) *Anal. Chem.* **78**, 2853–2858
- (73) Morales-Munoz, S., Luque-Garcia, J., & Luque de Castro, M. (2006) *Anal. Chim. Acta* **557**, 278–286
- (74) Cobb, J., Mattice, J., Senseman, S., Dumas, J., Mersie, W., Riley, M., Potter, T., Muellor, T., & Watson, E. (2006) *J. AOAC Int.* **89**, 903–912
- (75) Zhu, X., Yang, J., Su, Q., Cai, J., & Gao, Y. (2005) *J. Chromatogr. A* **1092**, 161–169
- (76) Han, D.M., Fang, G.Z., & Yan, X.P. (2005) *J. Chromatogr. A* **1100**, 131–136
- (77) Hunt, C.E., Pasetto, P., & Ansell, R.J. (2006) *Chem. Commun.* **2006**, 1754–1756
- (78) Tamayo, F., & Martin-Esteban, A. (2005) *J. Chromatogr. A* **1098**, 116–123
- (79) Danielsson, C., Wibereg, K., Korytar, P., Bergek, S., Brinkman, U., & Haglund, P. (2005) *J. Chromatogr. A* **1086**, 61–70
- (80) Focont, J.F., Eppe, G., Scippo, M.L., Massart, A.C., Pirard, C., Maghuin-Rogister, G., & De Pauw, E. (2005) *J. Chromatogr. A* **1086**, 45–60
- (81) Scippo, M.L., Rybertt, S., Eppe, G., Massart, A.C., De Pauw, E., & Maghuin-Rogister, G. (2006) *Accred. Qual. Assur.* **11**, 38–43
- (82) Gizzi, G., Hoogenboom, L., Van Holst, C., Rose, M., & Anklam, E. (2005) *Food Addit. Contam.* **22**, 472–481
- (83) Jeong, S., Cho, J., Park, J., & Denison, M. (2005) *J. Anal. Toxicol.* **29**, 156–162
- (84) Ivanova, P., Stratiev, D., & Pavlova, A. (2006) *J. AOAC Int.* **89**, 735–739
- (85) Korytar, P., Covaci, A., Leonards, P., de Boer, J., & Brinkman, U. (2005) *J. Chromatogr. A* **1100**, 200–207
- (86) Pere-Trepat, E., Lacorte, S., & Tauler, R. (2005) *J. Chromatogr. A* **1096**, 111–122
- (87) Piccirilli, G., & Excandar, G. (2006) *Analyst* **131**, 1012–1020
- (88) Tiryaki, O., & Baysoyu, D. (2006) *Accred. Qual. Assur.* **10**, 550–553
- (89) Tahboub, Y., Zaateer, M., & Al-Talla, A. (2005) *J. Chromatogr. A* **1098**, 150–155
- (90) Ostroukhova, O., & Zenkevich, I. (2006) *J. Anal. Chem.* **61**, 442–451
- (91) Horwitz, W., & Albert, R. (2006) *J. AOAC Int.* **89**, 1095–1109
- (92) Melo, L., Collins, C., & Jardim, I. (2005) *J. Chromatogr. A* **1073**, 75–81
- (93) Cacho, C., Turiel, E., Martin-Estaban, A., Ayala, D., & Perez-Conde, C. (2006) *J. Chromatogr. A* **1114**, 255–262
- (94) Ferrer, C., Gomez, M.J., Garcia-Reyes, J.F., Ferrer, I., Thurman, E.M., & Fernandez-Alba, A.R. (2005) *J. Chromatogr. A* **1069**, 183–194
- (95) Ferrer, I., & Thurman, M. (2006) *Chem. Aust. R. Aust. Chem. Inst.* **73**, 10–13
- (96) Guardia-Rubio, M., Fernandez-De Cordova, M., Ayora-Canada, M., & Ruiz-Medina, A. (2006) *J. Chromatogr. A* **1108**, 231–239

- (97) Tudorache, M., Co, M., Lifgren, H., & Emneus, J. (2005) *Anal. Chem.* **77**, 7156–7162
- (98) Tudorache, M., & Emneus, J. (2006) *Biosens. Bioelectron.* **21**, 1513–1520
- (99) Pang, G.F., Fan, C.L., Liu, Y.M., Cao, Y.Z., Zhang, J.J., Li, X.M., Li, Z.Y., Wu, Y.P., & Guo, T.T. (2006) *J. AOAC Int.* **89**, 740–771
- (100) Pang, G.F., Liu, Y.M., Fan, C.L., Zhang, J.J., Cao, Y.Z., Li, X.M., Li, Z.Y., Wu, Y.P., & Guo, T.T. (2006) *Anal. Bioanal. Chem.* **384**, 1366–1408
- (101) Pang, G.F., Cao, Y.Z., Zhang, J.J., Fan, C.L., Liu, Y.M., Li, X.M., Jia, G.Q., Li, Z.Y., Shi, Y.Q., Wu, Y.P., & Guo, T.T. (2006). *J. Chromatogr. A* **1125**, 1–30
- (102) Pang, G.F., Fan, C.L., Liu, Y.M., Cao, Y.Z., Zhang, J.J., Fu, B.L., Li, X.M., Li, Z.Y., & Wu, Y.P. (2006) *Food Addit. Contam.* **23**, 777–810
- (103) Moreno, J.L., Liebanas, F.J., Frenich, A.G., & Vidal, J.L. (2006) *J. Chromatogr. A* **1111**, 97–105
- (104) Patel, K., Fussell, R.J., Hetmanski, M., Goodall, D.M., & Keely, B.J. (2005) *J. Chromatogr. A* **1068**, 289–296
- (105) Montemurro, N., Grieco, F., Lacertosa, G., & Visconti, A. (2005) *Food Addit. Contam.* **22**, 39–47
- (106) Murray, J., Kelly, K., & Salmons, J.L. (2006) “Gel Permeation Chromatography Cleanup for the Combined Analysis of Chlorinated Pesticides and Flame Retardants in Beef Fat,” *Pittcon Abstracts: 2300-5*
- (107) Hancock, P., Hetmanski, M., & Fussell, R.J. (2005) “Determination of OCS, PCBs and Synthetic Pyrethroids in Animal Fat,” Poster presented at *Florida Pesticide Workshop, 2005*, Waters Publication No. 720001275EN, available at <http://www.waters.com/posters>
- (108) Walker, A.N., Bush, P., Puritz, J., Wilson, T., Chang, E.S., Miller, T., Holloway, K., & Horst, M.N. (2005) *Integr. Comp. Bio.* **45**, 118–126
- (109) Mendez, M.V.R., De La Rosa, I.P., Marquez, A.J., & Ojeda, M.U. (2005) *Food Addit. Contam.* **22**, 23–30
- (110) Zhang, W.G., Chu, X.G., Cai, H.X., An, J., & Li, C.J. (2006) *Rapid Commun. Mass Spectrom.* **20**, 609–617
- (111) Ambrus, A., Fuzesi, I., Susan, M., Dobi, D., Lantos, J., Zakar, F., Korsos, I., Olah, J., Beke, B.B., & Katavics, L. (2005) *J. Environ. Sci. Health B* **40**, 297–339
- (112) Porzano, T., & Cadoppi, A. (2005) “30X Increased Sensitivity in the Analysis of Pesticides in Food by GC-Large Volume Splitless Technique,” *Thermo Electron Corp. Application Note 10110*, Milan, Italy
- (113) Halvorson, M.R., Harrison, T.M., & Chambers, L. (2006) “Fipronil Analysis from a Variety of Matrices by GC/XSD Following Post-Extraction Gel Permeation Chromatography Cleanup,” *Pittcon Abstracts 2006: 970-20*, OI Analytical Application Note 25570306
- (114) Haixia, Z., Hashi, Y., & Yaping, Q. (2006) *Mod. Sci. Instr.* **1**, 72–74
- (115) Attalah, Y., Gad, S., Dogheim, S., Hashem, F., & El-Sawi, S. (2006) *J. Food Agric. Environ.* **4**, Online ISSN No. 1459–0263
- (116) Janska, M., Tomanoiva, M., Hajslova, J., & Kocourek, V. (2006) *Food Addit. Contam.* **23**, 309–325
- (117) Halvorson, M.R. (2006) “Post-Extraction Gel Permeation Chromatography (GPC) Cleanup of Red Pepper Prior to Analysis for Sudan Dyes,” *Pittcon Abstracts 2006:1850–35*, OI Analytical Application Note 25420206
- (118) Hatano, K. (2006) *J. Agric. Food Chem.* **54**, 562–567
- (119) Stark, T., Bareuther, S., & Hofmann, T. (2005) *J. Agric. Food Chem.* **53**, 5407–5418
- (120) Ozaki, A., Yamaguchi, Y., Fujita, T., Kuroda, K., & Endo, G. (2005) *Food Addit. Contam.* **22**, 1053–1060