

Committee on Residues and Related Topics

Metals and Other Elements

MILAN IHNAT

Pacific Agri-Food Research Centre - Summerland,
Agriculture and Agri-Food Canada, PO Box 5000,
Summerland, British Columbia, V0H 1Z0, Canada, Tel:
250-494-6411, Fax: 250-494-0755; E-mail:
ihnmatm@agr.gc.ca

Summary

This is the 13th report of the General Referee covering developments during the past year, presenting selected reports, and concluding with recommendations for consideration by the Methods Committee on Residues and Related Topics.

Selected Study Director Topics

Topic Advisor Milan Ihnat submitted a report summarizing progress in 4 areas, 3 study topics: Atomic Absorption Spectrometry; Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Atomic Emission Spectrometry; Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Mass Spectrometry, and a fourth related topic: Reference Materials (*see* ref. 1 for previous report).

Atomic Absorption Spectrometry

The first publication phase under the topic of (flame) atomic absorption spectrometry (FAAS) has been expanded to include 4 proposed, related scientific papers on the following topics: (1) preparation of fundamental and working calibrants, (2) generalized development of a highly reliable flame atomic absorption spectrometric method for multielement determinations in biological materials, (3) specific application of this method to the determination of 10 major, minor, and trace elements in agricultural/food reference materials by acid decomposition-FAAS, and (4) a comprehensive review of FAAS methods of analysis.

Scientific papers on topics titled "Elemental Calibration Solutions for Atomic Absorption Spectrometry" and "Development of a Reliable Acid Decomposition-Direct Aspiration Flame Atomic Absorption Spectrometric Method for the Analysis of Biological Materials" have been completed and will be submitted to *J. AOAC Int.* A third paper on "Application of Acid Decomposition-Direct Aspiration Flame Atomic Absorption Spectrometry to the Elemental Characterization of Agricultural/Food Reference Materials in a Certification Campaign" is in preparation. All 3 are preludes

to the preparation (also in progress) of the fourth major publication, "Flame Atomic Absorption Spectrometric Methodologies for Food Analysis—A Review."

Review was updated of attributes of currently available definitive, reference, routine, field, official, unofficial, and recommended methods from AOAC INTERNATIONAL and other method-developing agencies and standards organizations as well as other sources as a basis for the formulation of method recommendations. This review will offer guidance for the development of a unified, comprehensive, multielement flame atomic absorption scheme of analysis of foods for a range of major, minor, and trace elements leading to a proposed full scale collaborative study.

Work has progressed on the selection of spectrometric parameters and the further selection and acquisition of a wide variety of food, feed, food supplements, and related biological materials, including reference materials, comprehensively covering all 9 sectors of the AOAC Food Matrix Triangle, to provide a very broad complement of matrixes for method testing. This collection of materials is composed of products encompassing extreme ranges of the dominant proximate constituents, fat, protein, and carbohydrate as well as other constituents such as dietary fiber, ash, and the usual major elements. In addition, these materials are expected to contain a wide range of major, minor, and trace analyte elements conducive to providing thorough testing of the candidate method. It was recommended in the previous report (1) that the topic of *Lead in Calcium Supplements* be discontinued and instead integrated with other topics. This is being done to the extent possible under several other topics and thus food supplement matrixes are being incorporated into the topic of *Atomic Absorption Spectrometry* as well into the following active study topics: *Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)*; *Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)*; *Neutron Activation Analysis (NAA)*.

Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Atomic Emission Spectrometry.—Study Directors Milan Ihnat, Pacific Agri-Food Research Centre-Summerland, Agriculture and Agri-Food Canada, Summerland, British Columbia V0H 1Z0, Canada, Tel: 250-494-6411, Fax: 250-494-0755, E-mail: ihnmatm@agr.gc.ca; Victor J. Boyko and Ralph E. Sturgeon, Chemical Metrology, Institute for National Measurement Standards, National Research Council of Canada, Ottawa, ON K1A 0R9, Canada, Tel: 613-993-6395, Fax: 613-993-2451, E-mail: Ralph.Sturgeon@nrc.ca. The initial planning phase of this study was continued with selection of elements, materials,

decomposition and measurement procedures to be investigated and method evaluation. Activities within this study are being integrated with studies on AAS and ICP-MS. Progress will be impacted by the retirement of Boyko. Boyko's competent, valued contributions, regarding the technique of emission spectrometry, offered to his institution and to this Study Director during past years are gratefully acknowledged.

Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Mass Spectrometry.—Study Directors Milan Ihnat, Lu Yang, and Ralph E. Sturgeon, Chemical Metrology, Institute for National Measurement Standards, National Research Council of Canada, Ottawa, ON K1A 0R9, Canada, Tel: 613-993-6395, Fax: 613-993-2451, E-mail: Ralph.Sturgeon@nrc.ca. The initial phase was continued with planning of the study including selection of elements, materials, decomposition and measurement procedures to be investigated, and method evaluation with required experimentation. Activities within this study are being integrated with studies on AAS and ICP-AES. Detection limits (DLs) for potential analyte elements of interest were amassed as determined in the NRC laboratory using 2 different instruments, a Perkin-Elmer SCIEX ELAN 6000 quadrupole ICP mass spectrometer and a Thermo Electron Element 2 magnetic sector ICP mass spectrometer. Data were obtained under different conditions of low, medium, and high spectrometer resolution and using normal and cold argon plasmas. DLs are typically in the low ng/L (ppb) region down to an impressive 0.00001 ppb for Li. A cooler plasma, generated by using reduced radiofrequency power and increased argon injector flow rate, yields lower temperatures in the analyte sampling zone with perhaps substantially reduced polyatomic argide interferences. A comprehensive table of isobaric and polyatomic interferences on analytes of interest was surveyed to highlight an initial selection of preferred isotopes to be used for measurements in the proposed biological matrixes in light of the expected levels of the major (interfering) elements, Na, K, Ca, Mg, and Cl originating from the matrixes and bulk reagents used for decomposition and solution preparation.

Integration of Multi-Method Development Activities.—Analytical method developmental work on FAAS, ICP-AES, and ICP-MS is being coordinated and integrated with activities on instrumental (INAA) and radiochemical separation (RNAA) neutron activation analysis reported below. Thus, pooling of efforts on the topics *Flame Atomic Absorption Spectrometry (FAAS)*; *Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)*; and *Elements in Foods, Feeds, Food Supplements and Biological Materials by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)*, and *Neutron Activation Analysis* is expected to eventually yield several integrated, comprehensive, multielement analytical methods for foods and biological materials involving the 5 techniques of FAAS, ICP-AES, ICP-MS, INAA, and RNAA.

Reference Materials

Scientific and technical information continues to be disseminated in support of the formal agreement between Agriculture and Agri-Food Canada (AAFC), Ottawa, Canada, and the National Institute of Standards and Technology (NIST), Gaithersburg, MD, relating to 12 agricultural/food reference materials for elemental data analytical quality control, developed by the Study Director. The Study Director continues his role within the Technical Division on Reference Materials as liaison to the Methods Committee on Feeds, Fertilizers, and Agricultural Related Topics and member of the Reference Materials Methods Matching Committee. A Technical Report comprehensively documenting the entire AAFC/NIST Reference Material development program is in preparation.

Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods.—Study Director Nancy J. Miller-Ihli, Nutrient Composition Laboratory, Beltsville Human Nutrition Research Center, U.S. Department of Agriculture, Building 161, BARC-East, Beltsville, MD 20705, Tel: 301-504-8252, Fax: 301-504-8314, E-mail: miller-ihli@bhnrc.usda.gov. Study Director has retired. There has been no further work on this topic. Appreciation is expressed to Miller-Ihli for her years of service as Associate Referee on this topic as well as on the topic of *Graphite Furnace Atomic Absorption Spectrometric Determination of Lead in Sugar and Sugar Products*, discontinued last year, developing and publishing methods, gaining official status.

Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Released from Ceramicware.—This topic was discontinued last year. Appreciation is recorded to Study Director Susan C. Hight for her years of service as Associate Referee on this topic developing and publishing methods, gaining official status.

Lead in Wines.—Study Director Alan L. Reisig reported that there was no new communication from AOAC regarding the status and possibility of bringing this study to completion. It was previously reported that activity on the collaborative study "Determination of Lead in Beverage Alcohol Using Graphite Furnace Atomic Absorption Spectrometry" was on hold pending resolution of AOAC collaborative study funding issues. No indication was received by the General Referee from AOAC on the status of the funding situation and the previously submitted revised report containing additional statistical analysis.

Neutron Activation Analysis.—The topic is being continued with the joint appointment, reported previously, of Borut Smodis (Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia, E-mail: Borut.Smodis@IJS.SI) and Jan Kucera (Nuclear Physics Institute, Academy of Sciences of the Czech Republic, CZ-250 68 Rez near Prague, Czech Republic, Tel: 42-2-66172268, Fax: 42-2-6857003, E-mail: Kucera@ujf.cas.cz) as Topic Advisors. These established and recognized experts in the 2 major subdivisions of neutron activation analysis, namely, INAA and RNAA, are

cooperatively pursuing official method development involving one or both of these techniques. Progress has been thus far centered on discussions and initial study planning stages dealing with selection of elements, materials, and measurement procedures to be investigated. Detailed work planning discussions were held during summer 2005 to firm up experimental approaches. As activities within this study are being integrated with studies on AAS, ICP–AES, and ICP–MS, neutron activation studies will benefit from elemental, material, and methodological considerations formulated in these other studies.

Metals in Foods by Atomic Absorption Spectrometry.—Method Advisor Lars Jorhem reported that a specific-case limitation has been found for iron in the use of the dry ash Method 999.11 (also designated as NMKL No. 139). When applied to the determination of iron in fruit and vegetables preserved in tin cans, any tin present in the sample solution will precipitate because no hydrochloric acid is present. The result from a proficiency study using a canned product as test material gave a *z*-score of –8 (assigned value 60 mg/kg; found mean 16 mg/kg). Further studies have shown that iron coprecipitates with the tin when the ash is dissolved in 0.1 M nitric acid. No coprecipitation of Cd or Pb has been noted. This is, admittedly, a rather special case because tin and iron would most likely be determined after dissolution of the ash in hydrochloric acid. Good results are obtained for both Fe and Sn when the ash is dissolved in HCl but that version of the method is not yet validated or accredited by NMKL.

Total Mercury in Food by Cold Vapor Atomic Absorption Spectrometry.—Topic Advisor Robert W. Dabeka reported continued good success with development and real-life applications of a cold vapor atomic absorption method for mercury using the CETAC M6000-A mercury analyzer. The method for total mercury (2) was applied to total diet samples (3) and to edible fish and shellfish (4). In addition, it has been regularly applied to fish in a check sample program organized by the Canadian Food Inspection Agency. Results of the check sample program were always statistically satisfactory but in some instances biased high. Method performance was reviewed by comparing microwave sample digestion with the low temperature procedure in the method. Results from both digestions were identical indicating that the degree of destruction of organic matter does not impact the accuracy of the dedicated mercury analyzer. The method is still subject to potential loss of the blank in the absence of sample at solution concentrations <10 pg/mL. This will result in a positive bias for mercury in samples containing <1 ng/g. The method is expected to be available soon for validation study.

Recommendations

(1) *Atomic Absorption Spectrometry.*—Topic Advisor Milan Ihnat. Submit to *J. AOAC Int.* the manuscripts, “Elemental Calibration Solutions for Atomic Absorption Spectrometry” and “Development of a Reliable Acid Decomposition–Direct Aspiration Flame Atomic Absorption

Spectrometric Method for the Analysis of Biological Materials”; complete preparation of reports, “Application of Acid Decomposition–Direct Aspiration Flame Atomic Absorption Spectrometry to the Elemental Characterization of Agricultural/Food Reference Materials in a Certification Campaign” and “Flame Atomic Absorption Spectrometric Methodologies for Food Analysis—A Review.” Complete development of a proposed unified FAAS scheme of analysis of foods, feeds, food supplements, and biological materials for a range of elements and submit for collaborative study approval and publication in *J. AOAC Int.* Coordinate these developments on FAAS with ICP–AES, ICP–MS, and INAA/RNAA methods reported below. Continue study.

(2) *Elements in Foods, Feeds, Food Supplements, and Biological Materials by Inductively Coupled Plasma–Atomic Emission Spectrometry.*—Topic Advisors Milan Ihnat and Ralph E. Sturgeon. Complete the planning phase of this study with selection of elements, materials, decomposition, and measurement procedures to be investigated and delineation of methodological details. Integrate activities with concurrent studies on AAS and ICP–MS. Continue study.

(3) *Elements in Foods, Feeds, Food Supplements, and Biological Materials by Inductively Coupled Plasma–Mass Spectrometry.*—Topic Advisors Milan Ihnat, Lu Yang, and Ralph E. Sturgeon. Complete the planning phase of this study with selection of elements, materials, decomposition, and measurement procedures to be investigated and delineation of methodological and experimental details. Carry out preliminary determinations on a variety of digested matrixes, assessing practical DLs and isobaric and polyatomic interference corrections required for potential analyte elements of interest using quadrupole and magnetic sector ICP mass spectrometers, different spectrometer resolutions, and different argon plasmas. Integrate activities with concurrent studies on AAS and ICP–AES. Continue study.

(4) *Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods.*—Study Director Nancy J. Miller-Ihli. Due to the retirement of Miller-Ihli it may not be feasible to complete the collaborative study or peer validation on the graphite furnace atomic absorption method for the determination of chromium in foods and biological materials, based on the method published (*J. AOAC Int.* (1992) 75, 354–359). Discontinue topic.

(5) *Lead in Wines.*—Study Director Alan L. Reisig, BATF Laboratory, 1401 Research Blvd, Rockville, MD 20850, Tel: 240-264-1436, Fax: 301-413-9463, E-mail: Alan.Reisig@ttb.gov. Complete revision of the collaborative study, “Lead in Beverage Alcohol, Graphite Furnace Atomic Absorption Spectrometric Method,” following additional statistical analysis carried out previously and resubmit modified method. Make a last concerted effort, with assistance of the General Referee, to settle the collaborative study evaluation funding issues and bring this study to a conclusion. Continue study.

(6) *Neutron Activation Analysis.*—Topic Advisors Borut Smodis and Jan Kucera. Continue with joint cooperative pursuit of method development involving one or both of the

techniques of INAA and RNAA. Complete initial study planning stages dealing with selection of elements, materials, and experimental measurement procedures to be investigated. Integrate activities within this study with studies on AAS and ICP-MS to benefit from elemental, material, and methodological considerations formulated in these other studies. Continue study.

(7) **999.10** *Lead, Cadmium, Zinc, Copper, and Iron in Foodstuffs, Atomic Absorption Spectrophotometry after Microwave Digestion.*—Method Advisor Lars Jorhem, National Food Administration, Box 622, S-751 26 Uppsala, Sweden, Tel: 46 18 17 55 00, Fax: 46 18 10 58 48, E-mail: lajo@slv.se. Continue monitoring any reports from users of the Official Methods. Continue topic.

(8) **999.11** *Determination of Metals in Foodstuffs, Atomic Absorption Spectrophotometry after Dry Ashing.*—Method Advisor Lars Jorhem. Consider whether a modification is required to the applicability statement for this method in light of recent observations by the Method Advisor of the interference of tin on iron determination in fruit and vegetables preserved in tin cans. Continue monitoring any reports from users of the Official Methods. Continue topic.

(9) *Total Mercury in Food by Cold Vapor Atomic Absorption Spectrometry.*—Topic Advisor Robert W. Dabeka, Food Research Division 2203D, Health Protection Branch, Health Canada, Ottawa, Ontario K1A 0L2, Canada, Tel: 613-957-0951, Fax: 613-941-4775, E-mail: Bob_Dabeka@hc-sc.gc.ca. Continue with research/development of method for total mercury in foods using determinative techniques of cold vapor AAS and pretreatment and digestion methods as may be required. Prepare a detailed version of the method for validation. Continue study.

References

- (1) Ihnat, M. (2005) *J. AOAC Int.* **88**, 341–345
- (2) Dabeka, R.W., Bradley, P., & McKenzie, A.D. (2002) *J. AOAC Int.* **85**, 1136–1143
- (3) Dabeka, R.W., McKenzie, A.D., & Bradley, P. (2003) *Food Addit. Contam.* **20**, 629–638
- (4) Dabeka, R., McKenzie, A.D., Forsyth, D.S., & Conacher, H.B.S. (2004) *Food Addit. Contam.* **21**, 434–440

Pesticides and Other Chemical Contaminants

DAVID SODERBERG

U.S. Environmental Protection Agency, OPP, HED, RRB3, Rm 821D, Crystal Mall II, 7509C, Ariel Rios Bldg, 1200 Pennsylvania Ave, Washington, DC 20460, Tel: +1-703-308-4137, Fax: +1-703-305-5147, E-mail: soderberg.david@epamail.epa.gov

Summary

A new topic needs to be added to this refereeship this year. This topic is *Ultra-trace method for pesticides in bottled soft drinks*. The Study Director is Paul Milne. The topic *Dioxins by GC/MS* remains vacant.

General Topic Review

This year the General Referee was involved in revising the pesticides chapter of the *Official Methods of Analysis* in preparation for publication of the 18th edition. Surplussed methods have been restored because the electronic edition can accommodate them. Many methods to be included in the pesticides chapter of the new edition are either entirely obsolete, or are old enough to contain significant anachronisms in the equipment lists and instructions. Methods still in use need to be updated. If you have a vested interest in any of these older pesticide methods, please look at the new OMA when it becomes available. If you still use any of the methods in this chapter, please consider performing a single laboratory method modification of such methods so that, once again, there is a chapter that is current and useful.

Virtually all of the single analyte methods have been replaced, in practice, by newer methods in the *Pesticide Analytical Manual*, Volume 2 (PAM 2), and are not likely to be used in any of the usual testing programs. Reader feedback on whether these old, single analyte methods should be retained in OMA or should be archived in some manner would be appreciated.

Two new monographs on pesticide analysis in food and one on pesticide analysis in water have been published this year. *Chromatographic Mass Spectrometric Food Analysis for Trace Determination of Pesticide Residues*, A. Fernandez-Albam, 2005, Elsevier, was written as Volume 43 of Wilson and Wilson's *Comprehensive Analytical Chemistry*. D. Watson wrote *Pesticide, Veterinary and Other Residues in Food*, 2004, CRC Press, Woodhead Publishing, Ltd., Cambridge, UK, and D. Barcelo and M.C. Hennion wrote *Trace Determination of Pesticides and Their Degradation Products in Water*, 2E, 2003, Elsevier, Amsterdam, The Netherlands, which is Volume 19 of *Techniques and Instrumentation in Analytical Chemistry*.

In addition, the 2nd edition of the 3-volume *Handbook of Food Analysis*, 2E, by Leo M.L. Nollet, 2005, CRC Press, was published this year. This reference contains chapters on the residues in determination of urea pesticides, organochlorine pesticides, carbamate pesticides, organophosphate pesticides, fungicides, herbicides, polychlorobiphenyls, and dioxins and dioxin-like PCB residues in food.

Another reference, *Rapid Methods*, by A. von Amerongen, D. Barug, and M. Lauwaars, 2005, Wageningen Academic Publishers, discusses immunoassays and quick tests for pathogenic bacteria, and includes chapters on dioxins, polybrominated biphenyl ethers, and pesticides. A small section is devoted to sampling effects on pesticide residues (pp 48–53).

Several useful reviews have been published this year (1–7). New methods published this year have been almost entirely dominated by methods using detection by gas chromatography/mass spectrometry (GC/MS) or liquid chromatography/tandem MS (LC/MS/MS). GC/MS methods generally use gel permeation chromatography (GPC), solid-phase extraction (SPE), solid-phase microextraction (SPME), or matrix solid-phase dispersion (MSPD) cleanup steps followed by fast chromatography, large volume injection chromatography, and MS, MS/MS, or time of flight (TOF)-MS techniques. LC/MS methods use similar quick cleanup procedures such as SPE, SPME, or stir bar absorptive extraction, followed by LC/MS/MS or LC/TOF/MS, etc. All of the interesting papers in this group contain useful modifications or advances in technique; however, the large number of papers based multiresidue procedures published this year precludes in-depth discussion of each.

These various GC/MS and LC/MS systems have created a more or less universal scheme of determination of pesticide residues, at least in low-fat foods. Although universal scheme can be used for single analyte methods, class analyses, and multiresidue analyses, the distinctions among these different types of analyses having become blurred. Because the removal of matrix can be minimized with these techniques, there is reason for increased concern about matrix effects on the results. Also, at least from an EPA perspective, the value of the single analyte methods described in PAM 2, is that all are radiovalidated in one manner or another, and all are specifically designed to include those metabolites of the analyte that are of regulatory importance. On the other hand, no multianalyte method seems ever to have been radiovalidated. Whether all metabolites of regulatory importance are captured in these multiresidue methods has been more a matter of “catch as catch can,” than of always explicitly targeting the important metabolites.

This merging of GC/MS and LC/MS techniques into one or 2 universal techniques creates new concerns, while at the same time offering a new opportunity for rationalization and harmonization of nearly all pesticide methods in a new and unanticipated way.

Matrix effects are a concern in many residue analyses, but can be especially important in LC/MS/MS procedures precisely because there is less matrix cleanup in these methods. A couple of articles this year have discussed these matrix effects (8–10).

Thin-layer chromatography continues to be used. Ambrus (11, 12) reported a multiresidue method using a variety of detection systems with sensitivity of 0.1–100 ng. Rezić (13) determined triazines in honey, and Cao et al. (14) determined fenitrothion, parathion, and imidacloprid in Chinese cabbage.

Capillary electrophoresis (CE) continued to have a presence. Hernandez-Borges et al. (15) used stacking techniques to improve the sensitivity of CE analyses for several pesticides, and Wuilloud et al. (16) used inductively coupled plasma (ICP)-MS as a detection system for CE. Stir bar absorption was combined with micellar electrokinetic capillary chromatography (MEKC) using a diode array detector by Juan-Garcia et al. (17). Perez-Ruiz (18)

determined organophosphates, and Shakulashvili et al. (19) determined various pesticides by MEKC.

Immunoassays have been used for determination cypermethrin and permethrin (20), iprovalicarb (21), cyclodienes (22), carbofuran (23), fenarimol (24), type II pyrethroids (25), and atrazine plus a dichlobenil degradation product, 2,6-dichlorobenzamide (26). A disposable acetylcholinesterase-based device was reported for organophosphate and carbamate residues (27). Molecularly imprinted polymers were used for determination of sulfonyleurea herbicides (28).

A few publications describe electrometric and spectrophotometric techniques. Ni et al. determined 3 organophosphates simultaneously in vegetables (29) and carbamates in water (30), using differential pulse stripping voltammetry. Nikolelis et al. (31) determined carbofuran in foods by electrochemical detection of acetyl cholinesterase inhibition in a flow injection apparatus. Snejdarkova et al. (32) also developed an electrochemical system to detect carbofuran and related carbamates by acetyl cholinesterase inhibition. Solna et al. (33) developed a 4-electrode sensor for pesticides using immobilized tyrosinase, peroxidase, acetyl cholinesterase, and butyl cholinesterase. Huang et al. (34) used an SnO₂ gas sensitive electrode to determine organophosphorus pesticides in foods. Malik et al. (35) determined zineb and ziram in foods by the ability of zinc to complex (1,2'-pyridylazo)-2-naphthol-naphthalene and by measuring absorbance of the complex at 550 nm.

Several papers used less common extraction techniques and are worth noting. Water is always a nice nonpolluting extractant. Luthje et al. (36) used pressurized hot water extraction, online liquid/liquid extraction across a membrane, and GC/MS to determine pesticides in grapes. Yang and Ding (37) tried steam distillation and GC/MS detection for extraction of residues of alkylphenol polyethoxylate surfactants (in pesticide formulations) from foods. Rissato et al. (38) used supercritical fluid extraction to determine pesticides in honey. Cloud point extraction was used to extract organophosphates from foods (39). Chlorinated hydrocarbons were extracted from milk by simple centrifugal extraction of the fat (40). Kristenson et al. (41) used MSPD to determine pesticides in a single insect but not in food. Analysis of such tiny samples seems an ideal application for MSPD.

Microwave-assisted solvent extraction of pesticides from foods was used by 4 investigators (42–45). In addition, solvent-free microwave extraction of essential oils was reported by Lucchesi et al. (46, 47). Because many pesticides seem to concentrate in the essential oils of certain crops, this latter technique may have special value for analyzing residues in those crops.

Several papers describe techniques used to extract pesticides and other contaminants from water. Wenzel et al. (48) used an accelerated solvent extraction device to perform rapid dialysis within the extraction cell of persistent pollutants that had been collected from water onto a membrane. Lambropoulou and Albanis (49) used hollow fiber

SPME to determine various pesticides from water, and Lambropoulou et al. (50) also performed single drop microextraction of organophosphate pesticides from water. Rodriguez et al. (51) used ordinary SPME, but with on-fiber silylation, to determine acidic herbicides in water. Finally, Dalvie et al. (52) did a comparative cost analysis of enzyme-linked immunosorbent assay (ELISA), SPE, and SPME for monitoring pesticides in water.

A new technique, 2 photon excitation microscopy, is worth mentioning because, although unlikely to have any direct use in regulatory residue analysis, it allows visualization of the local movement of contaminants in plants, and therefore should greatly increase our understanding of residue distribution in plants in the near future (53).

A series of articles have appeared this year on methods for dioxin and polychlorinated biphenyl (PCB) analysis from a European perspective. Three papers discussed developments in GC/MS methods (54–56); another compared cleanup procedures used with GC/MS determination (57). One paper addressed use of pressurized liquid extraction for extracting PCBs from fish (58), and another discussed use of microwave-assisted extraction of polybrominated diphenyl ethers (PBDEs) from mussels (59). Two discussed the use of 2-dimensional GC (60, 61). Six (62–67) discussed the CALUX bioassay (Chemical Activated Luciferase gene Expression), a patented system in which a cell is engineered with a luciferase reporter gene to respond to Ah receptor agonists. Another paper discussed a comparison of various engineered cell Ah receptor agonist bioassays for dioxins (68). One paper presented a survey of PBDEs in the foods consumed in the United States (69). Three papers discussed quality control of methods, interlaboratory comparisons of results, and interlaboratory/intermethod comparisons (70–72), and 2 papers reviewed determination of these compounds using MS techniques (73, 74).

Several papers have appeared on chiral separations of allethrin and triazole pesticides (75–77) and one on chiral separation of PCBs (78). Felix (79) reviewed the commercial stationary phases available for separation of chiral pesticides.

Several authors, especially Sobleva and Ambrus, closely examined various uncertainties in pesticide analyses. Sandermann reviewed the current state of knowledge of bound residues (80). Thurman et al. (81) suggested a confirmation scheme using combined LC-TOF and LC/MS/MS results, and applied it to identification of metabolites (82). Sobleva and Ambrus (83) examined existing criteria for MS identification of pesticides and reported that these criteria led to too many false-negative results. Sobleva and Ambrus (84) also reported on a test to provide ongoing quality assurance of analytical system suitability for pesticide residue analysis. Ambrus and Sobleva (85) reported on the contribution of sampling to the uncertainty of pesticide residue results. A paper by Ambrus (86) addressed the major sources of error in pesticide analysis of foods and a paper by Sobleva et al. (87) reported the effects of having to measure multiple peaks on the uncertainty of certain pesticide measurements. Gonzalez et al. (88) used ongoing quality assurance records to assess ruggedness of

methods to small changes in analytical procedures. Although not a report on food analysis, a report by Pepich et al. (89) discussed stabilization of water samples for analysis of trace pesticide and flame retardant residues.

One paper described a procedure for simultaneous determination of dichlorvos, malathion, carbaryl, and 2,4-dichlorophenoxy acetic acid in citrus using direct injection in a tandem mass spectrometer, i.e., without any chromatographic separation (90).

A number of relative standard procedures and techniques were reported for various pesticides, and some interlaboratory studies were also described; however, these are not included here because this part of the report provides only an overview of highlights as seen by the General Referee. Although the review is not comprehensive, it is an AOAC report, and therefore includes all citations from *J. AOAC Int.* (91–104) and all pesticide residue citations attributed to our Method/Topic Advisors that are not listed elsewhere (105). These are all excellent papers that mostly were simply too mainstream to meet the criteria used by the General Referee for inclusion in this report. Note that any opinions expressed here are those of the General Referee and not those of the EPA.

Selected Study Director Topics

Chlorinated Dioxins

Topic Advisor Douglas Hayward, U.S. Food and Drug Administration (FDA), reports that PCB congener specific separations were investigated this year using a number of different columns. The results using fish fillet extract separations as a model were presented at Dioxin 2004 and were submitted for publication in *Chemosphere*. Four different columns were obtained including 5 or 5 ms phase columns (5% phenyl) from Agilent or Chrompak with a variety of sizes: 15–40 M, 0.18–0.25 mm id, higher temperature nonpolar (100 methyl silicone) Agilent DB-XLB column, SGE HT-8 (1,7-dicarbaclosedecarborane 8% phenyl) and a Supleco made SPB-octyl phase column. The SPB-octyl column has not been tested yet. It is specified in EPA 1614 for isomer specific determination of all 209 PCBs in environmental matrixes. The objective was to find a column that would separate the FDA list of 26 congeners and also be fast, reliable, and stable with fish extracts and other matrixes.

All 3 columns tested could separate many of the congeners. Only the DB-5 ms phase could separate all the target analytes, but none could separate all the target analytes from other coeluting congeners. The SGE HT-8 produced the best separations with fewest co-elutions. The 2 co-elutions of note were PCB77/149, a potential interference using either MS (HRMS) or MS/MS, and PCB 157/180, a problem for HRMS, but not a problem for MS/MS. All other targeted congeners were separated well past baseline and were generally separated less well on 5 ms phases or DB-XLB. PCB-77 will be separated from PCB 149 in the sample preparation and analyzed with the polychlorinated dibenzodioxin/furans (PCDD/Fs).

Progress has been made with the cleanup of difficult matrixes for PCBs (and PBDEs) such as fish oil, feed, green beans, and carrots. Several approaches were tested to purify PCDD/Fs, PCBs, and PBDEs in fish oil from the same test portion. A dual carbon approach with or without accelerated solvent extraction (ASE) with integrated cleanup showed some promise. Extracts that were clean enough to produce reliable chromatography and quantification tended to produce low recoveries of PCBs 52 and 101. This would compromise the results for PCBs 66, 74, 95, and 110 that were recovered better and are quantified using label PCB 52 or 101. A GPC setup was built for testing the fish oil cleanup instead. Four fish oil samples were successfully determined using GPC followed by alumina chromatography. Extracts for PCBs were relatively free of chromatographic noise or polyglow, and peak shapes were comparable to the standard, making quantification on the HT-8 or DB-XLB column easier. The DB-XLB column began losing GC resolution between important congeners after only a few fish extracts (PCBs 156/157; PCB 138/160), while HT-8 showed no such problem with fish fillets or fish oils.

The goal for the end of this year is to test with fish oil (and milk fat) and fish fillets, a dual approach for semi-automated cleanup of these matrixes for 50 analytes, including PCDD (7 congeners), PCDFs (10), PCBs (26), and PBDEs (7). The first approach for samples with 50–100% fat or for matrixes with interferences not removed by other means will go through automated GPC (1 g). Meanwhile a second larger aliquot (5–10 g) of the sample is passed through a disposable SPE custom-made carbon column for isolating PCDD/Fs and PCBs 77, 126, and 169.

In a second approach, matrixes like fish fillet, egg yolk, cheese, or any matrixes not needing GPC, will be placed in an ASE 300 cell with sulfuric acid silica gel, and extracted. The extract will be concentrated by chromatography over a disposable SPE custom-made carbon column with carbograph 1 (carbopak B or envirocarb equivalent) with an SCX column on top. PCDD/Fs and PCBs 77/126/169 will be isolated from the remaining PCBs and PBDEs by recovering them with toluene from the carbon and then eluting from alumina. PCBs and PBDEs may also need alumina chromatography. These 2 approaches will be tested with incurred fish fillet prepared by the conventional approach, fish oils and fortified test samples. PBDEs are determined by electron impact selected-ion monitoring (SIM) on an Agilent 5793 mass selective detector, whereas PCBs and PCDD/Fs are determined on a Saturn 4D or Saturn 2000 in MS/MS mode.

Determination of Residues of Triazines and Their Chlorometabolites in Raw Agricultural Commodities

Topic Advisor Robert Yokley. *Triazines in Raw Agricultural Commodities*.—Reports on the analysis of triazines in raw agricultural commodities were few in number from May 2004 through April 2005. Nonetheless, interesting and relevant papers were published in which the focus was primarily on sample preparation or, in some cases, the absence

or minimization of sample preparation. Methods are now dominated by the use of MS for final fraction analysis due to its high degree of sensitivity and selectivity, the need to obtain confirmatory identification of detected analytes, and its decreasing complexity of use.

A method based on MSPD sample preparation for the GC/MSD, SIM mode analysis of 7 triazines (15 compounds total) in carrot, grape, and multivegetable juices was reported (106). Juice samples of 1 mL volume were loaded onto 2 g quantities of Florisil™ contained in glass columns. A volume of 0.5 mL methanol (spiked methanol if used for procedural recovery purposes) was added to each sample. The columns (one-way stopcocks closed) were immersed in an ultrasonic bath and extracted twice with 5 mL ethyl acetate for 15 min at room temperature. The pooled extract was vacuum filtered and collected in a 10 mL graduated glass tube and concentrated to an appropriate volume (1 mL for the lowest fortification level used for recovery evaluation purposes) using a gentle stream of dry N₂ gas. The recoveries for simazine, atrazine, terbuthylazine, metribuzin, prometryn, terbutryn, and cyanazine ranged from 84 to 109% (vast majority in the 90s) with relative standard deviations (RSDs) ranging from 3 to 10% for concentration levels of 0.01–0.10 µg/mL. The reported lower limits of detection (LOD) ranged from 0.10 to 1.6 µg/L. For all analytes studied, sonication of the columns improved the recoveries. The extraction and cleanup can be performed in a single step, thus reducing the volume of organic solvent required for sample preparation.

In another application of MSPD, simazine, atrazine, and terbuthylazine and 9 other compounds (organophosphorus and halogen- and sulfur-containing compounds) were quantitatively determined in olives and olive oil using GC/MS and LC/MS/MS (107). A 1 g homogenized portion of olives (or 2 mL olive oil extract) was transferred to a glass mortar where it was gently blended with 2 g of 40 µm particle size aminopropyl (Bondesil-NH₂) until a fine powder was obtained. The mixture was then transferred to a minicolumn containing 2 g Florisil™ connected to an SPE vacuum manifold. Acetonitrile (2 × 5 mL) was used to elute the analytes at a flow rate of 3 mL/min. The final extract was evaporated until near dryness and reconstituted in 1 + 1 acetonitrile–water (for LC/MS) or acetonitrile (for GC/MS) after filtering through a 0.45 µm PTFE filter prior to analysis. Recoveries for simazine, atrazine, and terbuthylazine were 96, 81, and 86% at the method limit of quantitation (LOQ) of 10 µg/kg when LC/MS was used. The authors reported cleaner extracts and avoidance of fraction collection as in the use of GPC as well as minor solvent consumption and waste generation. Even small quantities of lipids can have deleterious effects on capillary columns and detectors and can cause signal suppression/enhancement issues in applications to high fat containing sample matrixes such as olives, olive oil, and avocados. In this work, signal suppression was as high as 35% for LC/MS and 15% for GC/MS measurements. This problem was circumvented by using matrix-matched standards for construction of the

calibration plots. Detection limits were reported as $<5 \mu\text{g}/\text{kg}$ using LC/MS and $10\text{--}60 \mu\text{g}/\text{kg}$ using GC/MS.

An automated on-line LC/GC procedure was reported for the determination of simazine and atrazine (as well as 6 other compounds) in olive oil (108). The biggest advantage of this procedure was the analysis of olive oil without sample preparation other than filtration through a $0.22 \mu\text{m}$ filter. On-line coupling combines the effectiveness of sample preparation during reversed-phase LC (RPLC) with the high efficiency and sensitivity of the GC portion of the measurement. An interface named TOTAD (through oven transfer adsorption-desorption) was used for on-line coupling of RPLC-GC. At a predetermined time after injection of $20 \mu\text{L}$ olive oil, switching valves diverted the LC flow from waste to the TOTAD interface, which consists of a glass liner packed with a 1 cm length of Tenax TA between 2 glass wool plugs. The analytes adsorbed to the Tenax TA while the solvent was vented by the flowing helium. After transfer of the analyte containing fraction to the TOTAD, the valves were again switched so that the LC flow was diverted back to waste. The interface was quickly heated to 250°C , leading to thermal desorption of the analytes which were subsequently carried into the GC column for separation and analysis using flame ionization detection. The total analysis time per sample was >54 min. Under reversed-phase conditions, the analytes were satisfactorily separated from the problematic triglyceride, squalene, and sterolic fractions, but procedural recoveries at $1 \text{ mg}/\text{L}$ for each compound were poor and ranged from 19 to 92% (all $<57\%$ except the 92% recovery). Good repeatability and sensitivity were achieved.

A highly selective immunoanalytical method for atrazine (and propazine) in extra virgin olive oil was developed (109) that involves direct extraction of the analyte from the oil with methanol followed by freeze-drying and plate or sensor immunoassay. Various olive oil samples were analyzed using these techniques as well as by GC/MS. Mean recoveries of 91% were obtained using polystyrene ELISA plates at fortification levels ranging from 10 to $500 \text{ ng}/\text{mL}$. These results compared well to those obtained using GC/MS, but the immunosensor results were enhanced by as much as 200% (mean 134%). The method may have potential for field applications because tedious extraction and cleanup procedures are not required.

A method for the analysis of simazine, atrazine, propazine, sebumeton, sebuthylazine, and desmetryn in bovine milk using hollow fiber membrane-protected (HFM) SPME GC/MS was described (110). Commercially available polypropylene HFM fibers were used as a sheath ($600 \mu\text{m}$ internal diameter) to accommodate and protect the SPME stainless steel tube housing the analytical SPME fiber. Bovine milk (5 mL) was mixed with sodium chloride (30%, w/v) and adjusted to pH 10 before transfer to a 10 mL long-neck vial. The HFM-SPME fiber was exposed to the sample solution for 40 min to attain extraction equilibrium (sample stirring was continuous at $130 \text{ rad}/\text{s}$). After this step, the SPME fiber was removed and gently wiped with soft tissue to remove water droplets. Thermal desorption of the analytes was achieved by

inserting the fiber into the GC injection port for 5 min. When the SPME fiber was used without the HFM to extract bovine milk, fatty material deposited in the GC column and peak tailing was observed. The recoveries and RSDs ranged from 88 to 107% and 2.8 to 9.8%, respectively, for all analytes at the $20 \mu\text{g}/\text{L}$ concentration level, but poor recoveries were obtained for simazine and atrazine (57 and 62%) at the $1 \mu\text{g}/\text{L}$ fortification level. In this work, the use of moderately polar polydimethylsiloxane (PDMS) divinylbenzene (DVB) fiber provided better efficiency than solely nonpolar PDMS fibers. Higher responses were observed at pH 10 and may be due to the hydrolysis of triazines at extreme acidic or basic pH. In addition, sample pH may play a role in reducing protein binding with the analytes. Higher sample extraction efficiencies were also observed with increased sodium chloride content up to about 30% due to protein and fatty sample component flocculation. Thus, milk samples do not need defatting and deproteinization prior to extraction. The procedure is not presently automated.

Quantitative recoveries and acceptable RSDs were obtained for atrazine, metribuzin, prometryn, and simazine as well as 94 other compounds at an LOQ of $0.01 \text{ mg}/\text{kg}$ when fruit-based baby food was analyzed using large volume-difficult matrix introduction-gas chromatography-time of flight-mass spectrometry (LV-DMI-GC-ToF-MS; 111). A 30 g portion of baby food was weighed into a 250 mL Duran Schott bottle followed by the addition of 60 mL ethyl acetate, $30\text{--}40 \text{ g}$ anhydrous sodium sulfate, and $5\text{--}6 \text{ g}$ sodium hydrogen carbonate. The bottles were heated to $30 \pm 3^\circ\text{C}$ for at least 20 min in a water bath. Afterwards, the samples were homogenized for 30 s. The upper layer was filtered through solvent-washed cotton wool and a 1 mL aliquot was transferred to a volumetric flask followed by reduction under a gentle stream of oxygen-free N_2 . A $50 \mu\text{L}$ volume of a $10 \mu\text{g}/\text{mL}$ internal standard of tetraphenylethylene was added and the final volume adjusted to 1 mL with ethyl acetate. In DMI, $10 \mu\text{L}$ extract is transferred to the DMI microvial where the volume is reduced to about $1 \mu\text{L}$ via automatically controlled venting of the solvent. The split line is closed and a temperature program results in transfer of the analytes into the GC capillary column followed by analysis using ToF-MS. Depending on their volatility, analytes transfer from the microvial to the GC as the temperature of the injector is increased; nonvolatile sample components remain in the microvial and do not contaminate the GC system. However, the higher acquisition rate of ToF mass analysis is needed because of the complexity of the chromatogram. Interferences were observed for a few compounds and in some cases the compounds were undetected. This may have been due to poor ionization or DMI transfer efficiency, active sites in the chromatography system, or problems with the sample extraction procedure. Retention time repeatability for LV-DMI-ToF-MS was comparable to that of splitless injection. Although the sample preparation procedure was simplified by eliminating a cleanup step, preconcentration of the extract was necessary to increase the number of compounds that could be quantified at $0.01 \text{ mg}/\text{kg}$. The run

time on a 30 m column was 25 min. More details of the instrumentation are described elsewhere (112).

A multiresidue method for the determination of >100 nitrogen, sulfur, and/or oxygen-containing pesticides (including 8 triazines) in fruits and vegetables using GC/MS was reported (113). Samples were subjected to the extraction and cleanup procedures already outlined in FDA's *Pesticide Analytical Manual*, Volume 1 (PAM 1), and analyzed using GC/MS in the SIM mode but including target and qualifier ions for only those compounds containing nitrogen, sulfur, and/or oxygen (NSOs). This was done because naturally occurring food components contain nitrogen or sulfur that are often co-extracted and detected by element-selective detectors. Plus, element-selective detection systems are considerably less sensitive for NSOs than phosphorus- or halogen-containing compounds. Using SIM in this manner increases the sensitivity and selectivity for the NSO compounds. Calculated LOQs [based on signal-to-noise (S/N) ratio considerations] for >100 NSOs ranged from 2 to 120 ng/g in orange pepper matrix (no cleanup). Twenty compounds were further studied in carrot, strawberry, lettuce, and pepper matrixes, and the calculated LOQs for terbutryn (the only triazine studied) were 2.4, 1.4, 2.2, and 4.2 ng/g, respectively, in these substrates. Note that recovery experiments at these calculated LOQ levels were not performed. Recoveries for terbutryn ranged from 91 to 103% in these substrates at the 25 and 500 ng/g concentration levels when the SPE step was included in the sample preparation procedure. Deuterated polycyclic aromatic hydrocarbons (PAHs) were used as internal standards in this work. On average, this method provides a 10-fold improvement in sensitivity for NSO compounds when compared with traditional element-selective detection systems.

A multiresidue screening procedure was described for the analysis of 73 compounds (including atrazine) in fruit and vegetables using LC/MS/MS (114). Frozen samples were milled and homogenized in dry ice. Subsamples (10 g) were shaken vigorously for 1 min with 10 mL acetonitrile followed by the addition of anhydrous magnesium sulfate and sodium chloride. The sample was immediately mixed on a Vortex mixer for 30 s. After centrifugation for 5 min, a 1 mL aliquot was transferred to a microcentrifuge vial containing 150 mg anhydrous magnesium sulfate, mixed, and centrifuged at $5200 \times g$ for 1 min. A 500 μ L portion of the extract was adjusted to a final fraction volume of 1 mL in water (crop concentration of 0.5 g/mL) for analysis using RPLC/MS/MS (TurboIonSpray™ in + mode). Two multiple reaction monitoring (MRM) transitions were used for each analyte, one for screening and one for confirmation, and the transitions were grouped into one of 3 acquisition time periods (0–18, 18–24, and 24–40 min). Matrix-matched standards were used for the construction of the calibration plots. Recoveries of 112, 88, and 106% with RSDs of 2, 6, and 7% were obtained for atrazine in orange, apple, and lettuce substrates, respectively, at an LOQ of 0.01 mg/kg.

Pesticides in Nonfatty Foods Using SFE and GC/MS

Study Director Steve Lehotay reported that AOAC Official Method **2002.03** was published in the new edition of the *Official Methods of Analysis* and approved Final Action. The collaborative study was published in *J. AOAC Int.* (2002) **85**, 1148–1166. The Study Director has received reprint requests for the publication and it has been cited in other publications.

Pesticides in Foods Using Acetonitrile Extraction and Partitioning with Magnesium Sulfate

Topic Advisor Steve Lehotay also reported that several new reports on the QuEChERS (which stands for quick, easy, cheap, effective, rugged, and safe) approach to pesticide residue analysis have been published (115–120).

Several other laboratories around the world have validated and implemented the QuEChERS method for the routine monitoring of pesticide residues. In November 2004, a 5-day training course was held at the USDA ARS Eastern Regional Research Center in Wyndmoor, PA, through the EPA for 17 chemists from U.S. state laboratories. In addition to training, the course also served to evaluate the QuEChERS method for different analysts using different labware over the course of 5 days. The method was successfully extended to dry foods and other matrixes, including soybeans, almonds, corn silage, molasses, pet food, alfalfa oats, foliage, and milk. Previously untested pesticides, such as thifensulfuron-methyl, were also evaluated in the training course. Results in nearly all cases were very good and statistically acceptable according to AOAC criteria.

The general QuEChERS protocol for the analysis of pesticide residues in foods, now entails: (1) Weigh 15 g high moisture sample (or 2 g dry sample + 13 mL water) in a 50 mL fluoroethylenepropylene (FEP) centrifuge tube; (2) add 15 mL 1% HAc in MeCN plus 6 g anhydrous MgSO₄ and 1.5 g anhydrous NaAc, and an internal standard solution; (3) shake for 1 min; (4) centrifuge at 3450 rcf for 1 min; (5) mix 1 mL extract with 150 mg anhydrous MgSO₄ + 50 mg primary secondary amine (PSA) + 50 mg C₁₈ sorbents for 20 s (dispersive-SPE approach); (6) centrifuge for 1 min at 3450 rcf; (7) transfer the extract to autosampler vials for concurrent analysis by GC/MS (with large volume injection) and LC/MS/MS. A vendor now commercially provides the dispersive-SPE format and a vortexing minicentrifuge can be used to combine steps 5 and 6.

The use of automated direct sample introduction with analyte protectants in GC/MS can provide strong benefits in the analysis of GC-amenable pesticides to lower detection limits, reduce matrix effects, improve quantitation, and increase ease and ruggedness. In the case of LC/MS/MS, the echo peak technique helps to ease quantitation, reduce matrix effects, and save time in the analysis.

The method gives typical recoveries of $95 \pm 10\%$ even for some problematic pesticides in nonfatty foods. In fatty matrixes, complete recoveries are also achieved for polar and semipolar pesticides, but partial recoveries were obtained for nonpolar pesticides depending on their lipophilicity and fat

content of the sample. For the most nonpolar pesticides, such as chlordane, consistent recoveries and low detection limits can still be achieved for samples up to 20% fat. Although recoveries of lipophilic pesticides are low when fat content is that high, if the samples are consistently the same percentage of fat, then results can be compensated for recoveries to yield accurate results.

In 2004, an international interlaboratory collaborative study was conducted to evaluate the QuEChERS method for pesticide residues in fruits and vegetables. In all, 13 laboratories in 7 countries provided results in the interlaboratory trial, which entailed 20 fortified pesticides at 3 levels between 10 and 1000 ng/g, plus 7 incurred residues, in 3 matrixes (grape, lettuce, and orange). Preliminary statistical review of all results was conducted according to AOAC criteria, and the results indicate that the method is acceptable for nearly all pesticides tested in each commodity. The Study Director is preparing the final report and will seek AOAC Official Method status for the method.

Miniaturized Methods

Associate Referee Frank Schenck, FDA, Atlanta, GA, used various SPE cleanups with the QuEChERS method for pesticides in fruits and vegetables. Briefly, this procedure entails extracting pesticides by mixing on a Vortex mixer with a 1% acetic acid–acetonitrile mix, salting out with sodium acetate and magnesium sulfate, and using a dispersive SPE cleanup (mixing on a Vortex mixer with PSA SPE sorbent and MgSO₄). This method did not provide a sufficient SPE cleanup, especially when used with the LC-post-column derivatization/fluorescence detection systems commonly used for carbamate pesticides. Two SPE cleanups for the QuEChERS method were evaluated: (1) A dispersive SPE cleanup using both PSA and graphitized carbon black (GCB) sorbents that had been developed at FDA-CFSAN; and (2) a cleanup using multilayer GCB/PSA SPE columns developed at FDA-Southeast Regional Laboratory. The combination of GCB and PSA provided an excellent cleanup, removing fatty acids, sterols, and plant pigments from the extract. The extracts could be used with LC-fluorescence and GC element selective detectors and MS detection systems. Problems previously encountered with recovery of planar aromatic pesticides from GCB were overcome. Using the QuEChERS method resulted in a 66–92% reduction in solvent usage and a 56–87% reduction in cost, compared to methods currently being used in our laboratories.

Synthetic Pyrethroids

Official Method **998.01** was adopted Final Action and was being published in the new edition of the OMA.

Multiresidue Methods by GC/MS and LC/MS

Topic Advisor Guo-Fang Pang advises that he has developed a set of 4 multiresidue pesticide methods in foods by GC/MS and LC/MS/MS. He is now in consultation with AOAC INTERNATIONAL and intends to perform a

collaborative study of one of the procedures. The 4 new methods are described below.

Simultaneous determination of 446 pesticide residues in fruits and vegetables by 3-cartridge SPE/GC/MS and LC/MS/MS.—A new method has been established for the simultaneous determination of 446 pesticide residues in fruits and vegetables using a 3-cartridge SPE cleanup with GC/MS and LC/MS/MS determination. This technique was based upon an assessment of the GC/MS and LC/MS/MS characteristics of 654 pesticides, the efficiency of extracting these residues from fruits and vegetables, and the ability to clean up the resulting extracts. From each fruit or vegetable a 20 g sample was extracted with 40 mL acetonitrile, salted out, and centrifuged. Half of each supernatant solution was loaded onto an Envi-18 cartridge, eluted with acetonitrile, concentrated, and cleaned up with tandem Envi-Carb and Sep-Pak NH₂ cartridges. Pesticides were eluted from these cartridges with acetonitrile + toluene (3:1, v/v) and eluates were concentrated to 0.5 mL. After solvent exchange with 2 × 5 mL hexane, internal standards were fortified into these solutions and 383 pesticides were determined by GC/MS. The other half of each supernatant was concentrated to 1 mL and cleaned up using tandem Envi-Carb and Sep-Pak NH₂ cartridges. Pesticides were eluted from these cartridges with acetonitrile + toluene (3:1, v/v). The eluates were concentrated to 0.5 mL, dried with nitrogen gas, diluted to 1.0 mL with acetonitrile + water (3:2, v/v) and 63 pesticides were determined in them by LC/MS/MS. In the linear range of each pesticide, the linear correlation coefficient was $r \geq 0.990$. When recovery and precision assessments were carried out at 3 fortification levels of 0.001–2.400 mg/kg for 6 varieties of either fruits and vegetables, the average recoveries for 446 pesticides all fell within the range of 60–125%; and the RSD for 436 of 446 pesticides (97.8%) was $\leq 25\%$. The RSD for the remaining 10 of 446 pesticides (2.2%) fell within the range of 25–30%. The LODs for the method were in the range of 0.0002–0.6000 mg/kg. The method is applicable for determination of 446 pesticide residues in fruits and vegetables such as apples, pears, oranges, bananas, grapes, pineapples, kiwi, cabbage, tomatoes, cucumbers, green peppers, spinaches, cauliflowers, celeries, string beans, carrots, potatoes, and lettuces.

Determination of 405 pesticides in grains by accelerated solvent extraction and SPE/GC/MS and LC/MS/MS.—A new method has been established for simultaneous determination of 405 pesticide residues in grains using accelerated solvent extraction and SPE with determination by GC/MS and LC/MS/MS. This method was based on an assessment of the GC/MS and LC/MS/MS characteristics of 654 pesticides, the efficiency of extracting these residues from grains, and ability to clean up the extracts. Grain samples (10 g) were mixed with 10 g Celite 545, placed into a 34 mL cell of the accelerated solvent extractor, and extracted with acetonitrile in the static state for 3 min, cycling twice under 10.34 MPa at 80°C. For 362 pesticides, half of each extract was cleaned up on an Envi-18 cartridge, and then loaded onto tandem Envi-Carb and Sep-Pak NH₂ cartridges. Pesticides were eluted from

these tandem cartridges with acetonitrile + toluene (3:1, v/v), concentrated, twice solvent-exchanged with hexane, fortified with an internal standard, and determined by GC/MS. For 43 pesticides, the other half of each extract was also cleaned up using a Sep-Pak Alumina N cartridge and then was loaded onto tandem Envi-Carb and Sep-Pak NH₂ cartridges. Pesticides were eluted from these tandem cartridges with acetonitrile + toluene (3:1, v/v). After evaporation to dryness, the eluates were diluted with acetonitrile + water (3:2, v/v) and analyzed by LC/MS/MS. In the linear range of each pesticide, the linear correlation coefficient was $r \geq 0.99$. At low, medium, and high fortification levels (at the LOD, 2 \times the LOD, and 8 \times the LOD), recoveries ranged from 40 to 130%. Recoveries of 386 of 405 pesticides (95.3%) ranged from 60 to 120%, recoveries of 11 of 405 pesticides (2.7%) ranged from 40 to 60%, and 8 of 405 pesticides (2.0%) ranged from 120 to 130%. The RSDs of these recoveries all fell below 35%, with 386 of 405 pesticides (95.3%) <25%, and 19 of 405 pesticides (4.7%) between 25 and 35%. The LODs were in the range 0.0002–0.3000 mg/kg. This method is applicable for determination of 405 pesticide residues in grains such as maize, wheat, oat, rice, and barley.

Simultaneous determination of 437 pesticide residues in animal tissues by GPC cleanup/GC/MS and LC/MS/MS.—A new GPC cleanup/GC/MS and LC/MS/MS method has been established for simultaneous determination of residues of 437 pesticides in the tissues of animals such as cows, sheep, pigs, chickens, and rabbits. This method was based on an assessment of the characteristics of both GC/MS and LC/MS/MS of 654 pesticides, the efficiency of extracting them from the animal tissues, and the ability to clean up the resulting extracts. Animal samples (5 g) were extracted with a mixture of cyclohexane + ethyl acetate (1:1, v/v). After concentration, the extracts were cleaned up on GPC Bio-beads S-X3 at a flow rate of 5 mL/min of cyclohexane + ethyl acetate (1:1, v/v), and the fractions eluting at 22–40 min were collected. For 374 pesticides, fractions were collected from the GPC, concentrated to 0.5 mL, solvent-exchanged twice with 5 mL hexane, and residues were determined by GC/MS. For 69 pesticides, the fractions collected from GPC were dried under nitrogen, dissolved in acetonitrile + water (60:40, v/v), and residues were determined by LC/MS/MS. In the linear range of each pesticide, the correlation coefficient was $r \geq 0.99$. At the low, medium, and high fortification levels of 0.0002 to 4.8 mg/kg, all recoveries fell between 40 and 120%. Of 437 pesticides, 417 (95.4%) had recoveries between 60 and 120%, and another 20 pesticides (4.6%) had recoveries between 40 and 60%. The RSDs of the recoveries for all pesticides were <25%. The LODs for the method were between 0.0002 and 0.6000 mg/kg.

Simultaneous determination of 450 pesticide residues in honeys by double-cartridge SPE/GC/MS and LC/MS/MS.—A new method has been established for simultaneous determination of 450 pesticide residues in honeys using tandem 2-cartridge SPE, and detection by GC/MS and LC/MS/MS. This method was based on an assessment of the

GC/MS and LC/MS/MS characteristics of 654 pesticides, the efficiency of their extraction from honey, and the ability to clean up the extracts. Honey samples (15 g) were dissolved in water, extracted with dichloromethane, concentrated, loaded onto tandem Envi-Carb and Sep-Pak NH₂ cartridges, and eluted with acetonitrile + toluene (3:1, v/v). The eluates were concentrated to 0.5 mL. Pesticides to be determined by LC/MS/MS were solvent-exchanged with methanol and determined using an external standard. Pesticides to be determined by GC/MS were solvent-exchanged with hexane and analyzed using an internal standard. In the linear range of each pesticide, the linear correlation coefficient was $r \geq 0.990$. At the 3 fortification levels of 0.004 and 1.200 mg/kg, the average recoveries fell within 51.6–114.6%. Of 450 pesticides, 432 (96.0%) had recoveries of 60–114.6%, and 18 (4.0%) had recoveries between 51.6 and 60%. Of 450 pesticide residues, 428 (95.1%) had RSDs <25%, and 22 of 450 pesticide residues (4.9%) had RSDs between 25 and 37.2%. The LODs for the method ranged between 0.001 and 0.300 mg/kg.

Ultra-Trace Method for Pesticides in Bottled Soft Drinks

Study Director Paul Milne reports that 2 methods have been developed and are currently undergoing preliminary testing prior to a collaborative study. AOAC staff have accepted this method for the performance of a collaborative study.

In the first method pesticide residues are extracted from soft drinks by partition with dichloromethane. The partition is repeated twice more and the combined organic fractions are concentrated to near dryness and reconstituted in hexane. The hexane fraction is further partitioned against water made basic with sodium hydroxide. The concentration of the analytes in the final extracts is determined by capillary GC/MS.

A second method allows for determination of additional pesticides. In this procedure the liquid matrixes are centrifuged and filtered to remove particulate matter, with no further cleanup. Determination is performed by HPLC using MS/MS for detection.

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: +1-301-436-1654, Fax: +1-301-436-2632, e-mail: douglas.hayward@cfsan.fda.gov. This topic has been very active this year. Continue topic.

(2) *Determination of Residues of Triazines and Their Chlorometabolites in Raw Agricultural Commodities.*—Topic Advisor Robert Yokley, Syngenta Crop Protection, Inc., PO Box 18300, Greensboro, NC 27409, Tel: +1-336-632-2142, Fax: +1-336-632-7645, e-mail: Robert.yokley@syngenta.com. The Topic Advisor is bringing new life to this topic. Continue topic.

(3) **2002.03 Pesticides in Nonfatty Foods Using SFE and GC/MS.**—Study Director Steven J. Lehotay, U.S. Department of Agriculture, ARS ERRC, 600 E. Mermaid Ln, Wyndmoor, PA 19038, Tel: +1-215-233-6433, Fax: +1-215-233-6642, e-mail: slehotay@errc.ars.usda.gov. This method has been approved Final Action and was published in the new edition of OMA. Recommend continue topic until the method has been available through OMA at least 1 year.

(4) **Pesticides in Foods Using Acetonitrile Extraction and Partitioning with Magnesium Sulfate.**—Topic Advisor 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: +1-404-253-1200, Fax: +1-404-253-1208, e-mail: fschenck@ora.fda.gov. This topic area is very active with investigations ongoing into SPE to reduce matrix effects. 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, Qinhuangdao, People's Republic of China, Tel/Fax: 86-335-341-7119; e-mail: panggfciq@pang.com.cn. Adopted as Final Action with Comments May 2003. Continue monitoring any reports from users of Official Method **998.01** for at least 1 year after publication in the new edition of *Official Methods of Analysis*.

(7) **Multiresidue Methods for Pesticides in Foods by GC/MS and LC/MS/MS.**—Topic Advisor Guo-Fang Pang. This topic is very active and is expected to soon lead to a proposed collaborative study. Initiate topic.

(8) **Ultra-Trace Method for Pesticides in Bottled Soft Drinks.**—Study Director Paul Milne, Pepsi Cola Co, Valhalla, NY 10595, Tel: +1-914-742-4743, Fax: +1-914-749-3323, e-mail: pmilne@pepsi.com. Methods have been developed and are currently undergoing preliminary testing prior to a collaborative study. Initiate topic.

References

- (1) Koester, C. (2005) *Anal. Chem.* **77**, 3737–3754
- (2) Andreu, V., & Pico, Y. (2004) *Trends Anal. Chem.* **23**, 772–788
- (3) Hernandez, F., Pozo, O., Sancho, J., Lopez, F., Marin, J., & Ibanez, M. (2005) *Trends Anal. Chem.* **24**, 596–612
- (4) Nunez, O., Moyano, E., & Garceron, M. (2005) *Trends Anal. Chem.* **24**, 683–703
- (5) Richardson, S. (2004) *Anal. Chem.* **76**, 3337–3364
- (6) Ferrer, I., Garcia-Reyes, J., & Fernandez-Alba, A. (2005) *Trends Anal. Chem.* **24**, 671–682
- (7) Carabias-Martinez, R., Rodriguez-Gonzalo, E., Revilla-Ruiz, P., & Hernandez-Mendez, J. (2005) *J. Chromatogr. A* **1089**, 1–17
- (8) Mei, H., & Korfmacher, W. (2005) *Using Mass Spectrometry for Drug Metabolism Studies*, CRC Press, Boca Raton, FL, pp 103–150
- (9) Taylor, P. (2005) *Clin. Biochem.* **38**, 328–334
- (10) Souverain, S., Rudaz, S., & Venthey, J.L. (2004) *J. Chromatogr. A* **1058**, 61–66
- (11) Ambrus, A. (2005) *J. Environ. Sci. Health B Pestic. Food Contam. Agric. Wastes* **40**, 297–339
- (12) Ambrus, A. (2005) *J. Environ. Sci. Health B Pestic. Food Contam. Agric. Wastes* **40**, 485–511
- (13) Rezic, I. (2005) *Ultrason. Sonochem.* **12**, 477–481
- (14) Cao, H., Yue, Y., Hua, R., Tang, F., Zhang, R., Fan, W., & Chen, H. (2005) *J. Planar Chromatogr.* **18**, 151–154
- (15) Hernandez-Borges, J., Cifuentes, A., Garcia-Montelongo, F., & Rodriguez-Delgado, M. (2005) *Electrophoresis* **26**, 980–989
- (16) Wuilloud, R., Shah, M., Kannamkumarath, S., & Altamirano, J. (2005) *Electrophoresis* **26**, 1598–1605
- (17) Juan-Garcia, A., Pico, Y., & Font, G. (2005) *J. Chromatogr. A* **1073**, 229–236
- (18) Perez-Ruiz, T., Martinez-Lozano, C., Sanz, A., & Bravo, E. (2005) *Chromatographia* **61**, 493–498
- (19) Shakulashvili, N., Reviz, R., Steiner, F., & Engelhardt, H. (2004) *Chromatographia* **60**, 145–150
- (20) Park, E.K., Kim, J.H., Gee, S., Wayanabe, T., Ahn, K., & Hammock, B. (2004) *J. Agric. Food Chem.* **52**, 5572–5576
- (21) Lee, J., Park, S., Lee, E., Kim, Y., & Kyong, K. (2004) *J. Agric. Food Chem.* **52**, 6680–6686
- (22) Manclus, J., Abad, A., Lebedev, M., Mojarrad, F., Mickova, B., Mercader, J., Primo, J., Miranda, M., & Montoya, A. (2004) *J. Agric. Food Chem.* **52**, 2776–2784
- (23) Zhou, P., Lu, Y., Zhu, J., Hong, J., Li, B., Zhou, J., Gong, D., & Montoya, A. (2003) *J. Agric. Food Chem.* **52**, 4355–4359
- (24) Lee, J., Park, S., Lee, E., Kim, Y., & Kyung, K. (2004) *J. Agric. Food Chem.* **52**, 7206–7213
- (25) Mak, S., Shan, G., Lee, H.J., Watanabe, T., Stoutamire, D., Gee, S., & Hammock, B. (2005) *Anal. Chim. Acta* **534**, 109–120
- (26) Belleville, E., Dufva, M., Aamand, J., Bruun, L., Clausen, L., & Christensen, C. (2004) *J. Immunol. Methods* **286**, 219–229
- (27) Zhang, Y., Muench, S., Schulze, H., Perz, R., Yang, B., Schmidt R., & Bachmann, T. (2005) *J. Agric. Food Chem.* **53**, 5110–5115
- (28) Bastide, J., Cambon, J.P., Breton, F., Piletsky, S., & Rouillon, R. (2005) *Anal. Chim. Acta* **542**, 97–103
- (29) Ni, Y., Qiu, P., & Kokot, S. (2004) *Anal. Chim. Acta* **516**, 7–17
- (30) Ni, Y., Qiu, P., & Kokot, S. (2005) *Anal. Chim. Acta* **537**, 321–330
- (31) Nikolelis, D., Simantiraki, M., & Siontorou, C., & Toth, K. (2005) *Anal. Chim. Acta* **537**, 169–177
- (32) Snejdarkova, M., Svobodova, L., Evtugyn, G., Budnikov, H., Karyakin, H., Nikolelis, D., & Hianik, J. (2004) *Anal. Chim. Acta* **514**, 79–88
- (33) Solna, R., Sapelnikova, J., Skladal, P., Winther-Nielson, M., Carlsson, C., Emneus, J., & Ruzgas, T. (2005) *Talanta* **65**, 349–357
- (34) Huang, X., Liu, J., Pi, Z., & Yu, Z. (2004) *Talanta* **64**, 538–545
- (35) Malik, A., Sharma, V., Sharma, V., & Rao, A. (2004) *J. Agric. Food Chem.* **52**, 7763–7767
- (36) Luthje, K., Hyotylainen, T., Rautainen-Rama, M., & Riekkola, M. (2005) *Analyst* **140**, 52–58

- (37) Yang, D.K., & Ding, W.H. (2005) *J. Chromatogr. A* **1088**, 200–204
- (38) Rissato, S., Galhiane, M., Knoll, F., & Apon, B. (2004) *J. Chromatogr. A* **1048**, 153–159
- (39) Sanz, C., Halko, R., Ferrera, Z., & Rodriguez, J. (2004) *Anal. Chim. Acta* **524**, 265–270
- (40) Armendariz, C., de Ciriza, J., & Farre, R. (2004) *Int. J. Food Sci. Nutr.* **55**, 215–221
- (41) Kristenson, E., Shahmiri, S., Slooten, C., Vreuls, R., & Brinkman, U. (2004) *Chromatographia* **59**, 315–320
- (42) Barriada-Pereira, M., Gonzalez-Castro, M., & Muniategui-Lorenzo, S. (2005) *Int. J. Environ. Anal. Chem.* **85**, 325–333
- (43) Singh, S., Foster, G., & Khan, S. (2004) *J. Agric. Food Chem.* **52**, 105–109
- (44) Gfrerer, M., & Lankmayr, E. (2005) *Anal. Chim. Acta* **533**, 203–211
- (45) Yusa, V., Pastor, A., & de la Guardia, M. (2005) *Anal. Chim. Acta* **540**, 355–366
- (46) Lucchesi, M., Chemat, F., & Smadja, J. (2004) *J. Chromatogr. A* **1043**, 323–327
- (47) Lucchesi, M., Chemat, F., & Samdja, J. (2004) *Flavour Frag. J.* **19**, 134–138
- (48) Wenzel, K.D., Vrana, B., Hubert, A., & Schurmann, G. (2004) *Anal. Chem.* **76**, 5503–5509
- (49) Lambropoulou, D., & Albanis, T. (2005) *J. Chromatogr. A* **1072**, 55–61
- (50) Lambropoulou, D., Psillakis, E., Albanis, T., & Kalogerakis, N. (2004) *Anal. Chim. Acta* **516**, 205–211
- (51) Rodriguez, I., Rubi, E., Gonzalez, J., Quintana, J., & Cela, R. (2005) *Anal. Chim. Acta* **537**, 259–266
- (52) Dalvie, M., Sinanovic, E., London, L., Cairncross, E., Soloman, A., & Adam, H. (2005) *Environ. Res.* **98**, 143–150
- (53) Wild, E., Dent, J., Barber, J., Thomas, G.O., & Jones, K. (2004) *Environ. Sci. Technol.* **38**, 4195–4199
- (54) Fernandez, A., White, S., D'Silva, K., & Rose, M. (2004) *Talanta* **63**, 1147–1155
- (55) Eppe, G., Focant, J.F., Pirard, C., & De Pauw, E. (2004) *Talanta* **63**, 1135–1146
- (56) Focant, J.F., Picard, C., Eppe, G., & De Pauw, E. (2005) *J. Chromatogr. A* **1067**, 265–275
- (57) Focant, J.F., Pirard, C., & De Pauw, E. (2004) *Talanta* **63**, 1101–1113
- (58) Suchan, P., Pulkrabova, J., Hajslova, J., & Kocourek, V. (2004) *Anal. Chim. Acta* **520**, 193–200
- (59) Bayen, S., Lee, H., & Obbard, J. (2004) *J. Chromatogr. A* **1035**, 291–294
- (60) Focant, 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
- (61) Korytar, P., Leonards, P., de Boer, J., & Brinkman, U. (2005) *J. Chromatogr. A* **1086**, 29–44
- (62) Scippo, M.L. (2004) *Talanta* **63**, 1195–1202
- (63) Van Overmeire, I., Van Loco, J., Roos, P., Carbonnelle, S., & Goeyens, L. (2004) *Talanta* **63**, 1241–1247
- (64) Carbonnelle, S., Van Loco, J., Van Overmeire, I., Windal, I., Van Wouwe, N., Van Leeuwen, S., & Goeyens, L. (2004) *Talanta* **63**, 1255–1259
- (65) Van Wouwe, N., Windal, I., Vanderperren, H., Eppe, G., Xhrouet, C., De Pauw, E., Goeyens, L., & Baeyens, W. (2004) *Talanta* **63**, 1269–1272
- (66) Schroijsen, C., Windal, I., Goeyens, L., & Baeyens, W. (2004) *Talanta* **63**, 1261–1268
- (67) Van Wouwe, N., Windal, J., Vanderperren, H., Eppe, G., Xhrouet, C., Massart, A.C., Debacker, N., Sasse, A., Baeyens, W., De Pauw, E., Sartor, F., Van Oyen, H., & Goeyens, L. (2004) *Talanta* **63**, 1157–1167
- (68) Denison, M., Zhao, B., Baston, D., Clark, G., Murata, H., & Han, D. (2004) *Talanta* **63**, 1261–1268
- (69) Schecter, A., Papke, O., Tung, K.C., Staskal, D., & Birnbaum, L. (2004) *Environ. Sci.* **38**, 5306–5311
- (70) Papke, O., Furst, P., & Herrmann, T. (2004) *Talanta* **63**, 1203–1211
- (71) Becher, G., Haug, L., & Thomsen, C. (2004) *Talanta* **63**, 1115–1122
- (72) Van Loco, J., Van Leeuwen, S., Roos, P., Carbonnelle, S., de Boer, J., Goeyens, L., & Beernaert, H. (2004) *Talanta* **63**, 1169–1182
- (73) Focant, J.F., Picard, C., Eppe, G., & De Pauw, E. (2005) *J. Chromatogr. A* **1067**, 265–275
- (74) Focant, J.F., Picard, C., & De Pauw, E. (2004) *Talanta* **63**, 1101–1113
- (75) Mancini, F., Fion, J., Bertucci, C., Cavrini, V., Bragieri, M., Zanotti, M., Liverani, A., Borzatta, V., & Andrisano, V. (2004) *J. Chromatogr. A* **1046**, 67–73
- (76) Wang, P., Jiang, S., Wang, P., & Zhou, Z. (2005) *J. Biochem. Biophys. Methods* **62**, 219–230
- (77) Toribio, L., del Nozal, M., Bernal, J., Jimenez, J., & Alonso, C. (2004) *J. Chromatogr. A* **1046**, 249–253
- (78) Bordajandi, L., Ramos, L., & Gonzalez, M. (2005) *J. Chromatogr. A* **1078**, 128–135
- (79) Felix, G. (2004) *J. Liq. Chromatogr. Rel. Technol.* **27**, 237–273
- (80) Sandermann, H. (2004) *Pest Manag. Sci.* **60**, 613–623
- (81) Thurman, E., Ferrer, I., & Fernandez-Alba, A. (2005) *J. Chromatogr. A* **1067**, 127–134
- (82) Thurman, E., Ferrer, I., Sweigenbaum, J., Garcia-Reyes, J., Woodman, M., & Fernandez-Alba, A. (2005) *J. Chromatogr. A* **1082**, 71–80
- (83) Sobleva, E., & Ambrus, A. (2004) *Analyst* **129**, 1123–1129
- (84) Sobleva, E., & Ambrus, A. (2004) *J. Chromatogr. A* **1027**, 55–65
- (85) Ambrus, A., & Sobleva, E. (2004) *J. AOAC Int.* **87**, 1368–1379
- (86) Ambrus, A. (2004) *Accredit. Qual. Assur.* **9**, 288–304
- (87) Sobleva, E., Ambrus, A., & Jarju, O. (2004) *J. Chromatogr. A* **1029**, 161–166
- (88) Gonzalez, F., Torres, M., Frenich, A., Vidal, J., & Campana, A. (2004) *Trends Anal. Chem.* **23**, 361–369
- (89) Pepich, B., Prakash, B., Domino, M., Dattilio, T., Munch, D., & Price, E. (2005) *Environ. Sci. Technol.* **39**, 4996–5004
- (90) Nakazawa, H., Takahashi, N., Inoue, K., Ito, Y., Goto, T., Kato, K., Yoshimura, Y., & Oka, H. (2004) *Talanta* **64**, 899–905
- (91) Wu, J., Li, L., & Zou, Y. (2005) *J. AOAC Int.* **88**, 1261–1264

- (92) Sanchez, R., Cortes, J., Villen, J., & Vazquez, A. (2005) *J. AOAC Int.* **88**, 1255–1260
- (93) Hwang, Y., Wong, Y., & Ho, W. (2005) *J. AOAC Int.* **88**, 1236–1241
- (94) He, J., Hou, X., Jiang, H., & Shen, J. (2005) *J. AOAC Int.* **88**, 1099–1103
- (95) Blasco, C., Font, G., Manes, J., & Pico, Y. (2005) *J. AOAC Int.* **88**, 847–853
- (96) Doran, G., Helliwell, S., & Eberbach, P. (2005) *J. AOAC Int.* **88**, 847–853
- (97) Laurent-Martinez, E., & Garcia-Reyes, J. (2005) *J. AOAC Int.* **88**, 860–865
- (98) Brown, P., Turnbull, G., Charman, S., Charlton, A., & Jones, A. (2005) *J. AOAC Int.* **88**, 204–220
- (99) Saito, Y., Kodama, S., Matsunaga, A., & Yamamoto, A. (2004) *J. AOAC Int.* **87**, 1356–1367
- (100) Wu, J., & Li, L. (2004) *J. AOAC Int.* **87**, 1260–1263
- (101) Hu, X., Jianxin, Y., Zhigang, Y., Lansun, N., Yanfei, L., Peng, W., Jong, L., Xin, H., Xiaogang, C., & Yibin, Z. (2004) *J. AOAC Int.* **87**, 972–985
- (102) Sannino, A. (2004) *J. AOAC Int.* **87**, 991–996
- (103) Ting, K.C., Zhou, E., & Saini, N. (2004) *J. AOAC Int.* **87**, 997–1002
- (104) Ueno, E., Oshimi, H., Saito, I., Matsumoto, H., Yoshimura, Y., & Nakazawa, H. (2004) *J. AOAC Int.* **87**, 1003–1015
- (105) Mastovska, K., Hajslova, J., & Lehotay, S. (2004) *J. Chromatogr. A* **1054**, 335–349
- (106) Albero, B., Sanchez-Brunete, C., Donoso, A., & Tadeo, J.L. (2004) *J. Chromatogr. A* **1043**, 127–133
- (107) 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
- (108) Sanchez, R., Vazquez, A., Andini, J.C., & Villen, J. (2004) *J. Chromatogr. A* **1029**, 167–172
- (109) Garces-Garcia, M., Morais, S., Gonzalez-Martinez, M.A., Puchades, R., & Maquiera, A. (2004) *Anal. Bioanal. Chem.* **378**, 484–489
- (110) Basheer, C., & Lee, H.K. (2004) *J. Chromatogr. A* **1047**, 189–204
- (111) Patel, K., Fussell, R.J., Goodall, D.M., & Keely, B.J. (2004) *Food Addit. Contam.* **21**, 658–669
- (112) De Koning, J.A., Lach, G., Linkerhagner, M., Loscher, R., Tablack, P.H., & Brinkman, U.A.T. (2003) *J. Chromatogr. A* **1008**, 247–252
- (113) Mercer, G.E., & Hurlbut, J.A. (2004) *J. AOAC Int.* **87**, 1224–1236
- (114) Hetherington, C.L., Sykes, M.D., Fussell, R.J., & Goodall, D.M. (2004) *Rapid Commun. Mass Spectrom.* **18**, 2443–2450
- (115) Lehotay, S.J., de Kok, A., Hiemstra, M., & van Bodegraven, P. (2005) *J. AOAC Int.* **88**, 595–614
- (116) Lehotay, S.J., Maštovská, K., & Lightfield, A.R. (2005) *J. AOAC Int.* **88**, 615–629
- (117) Lehotay, S.J., Maštovská, K., & Yun, S.J. (2005) *J. AOAC Int.* **88**, 630–638
- (118) Schenck, F.J., & Hobbs, J.E. (2004) *Bull. Environ. Contam. Toxicol.* **73**, 24–30
- (119) Ěajka, T., Maštovská, K., Lehotay, S.J., & Hajšlová, J. (2005) *J. Sep. Sci.* **28**, 1048–1060
- (120) Lehotay, S.J. (2005) in *Methods in Biotechnology, Pesticide Analysis*, J.L. Martinez-Vidal & G. Frenich (Eds), Humana Press, New York, NY, Chapter 19