Committee on Residues and Related Topics

Metals and Other Elements

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Selected Study Director Topics

Atomic Absorption Spectrometry

Study Director Milan Ihnat submitted a report summarizing progress in 2 areas, Atomic Absorption Spectrometry and Reference Materials, related to his Study Director topic.

Preparation of a comprehensive review on flame atomic absorption spectrometric (FAAS) methodologies for food analysis is in progress for *J. AOAC Int.* It encompasses a review of official and recommended AAS methods developed by AOAC INTERNATIONAL and other method-developing agencies and standards organizations as well as other sources of methods for elemental determination of individual or limited groups of elements especially in food matrixes but also in a variety of other relevant biological matrixes. 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. Development of the unified method and full scale collaborative study based on it are proposed to be completed in 2002. The following papers and reports related to AAS were presented and published:

(1) Ihnat, M., Neilsen, G.H., & Hogue, E.H. (2000) *Commun. Soil Sci. Plant Anal*. **31**, 803–825

(2) Ihnat, M. (2000) *Flame Atomic Absorption Spectrometric Methodologies for Food Analysis: A Review*, Final Program, 114th AOAC INTERNATIONAL Annual Meeting and Exposition, September 10–14, Philadelphia, PA, Abstract E-113

Reference Materials

Scientific and technical information relating to the 12 Agricultural/Food Reference Materials for elemental data analytical quality control, developed by the Study Director in a collaborative venture between Agriculture and Agri-Food Canada, Ottawa, and the National Institute of Standards and Technology (NIST), Gaithersburg, MD, continues to be disseminated. Additional scientific reports have been published and a technical report, comprehensively documenting the entire Reference Material development venture, is in preparation. Current work at NIST is geared to the characterization of a number of these RMs for other nutritional parameters such as proximate constituents, fatty acids and caloric value, and the updating and revision of Reports of Analyses. The following papers and reports, related to Reference Materials, were presented and published:

(1) Ihnat, M. (2000) *Book of Abstracts*, 8th International Symposium on Biological and Environmental Reference Materials (BERM-8), September 17–22, Bethesda, MD, Abstract p. 59, "Twenty-Five Years of Reference Material Activity at Agriculture and Agri-Food Canada"

(2) Ihnat, M. (2000) *Book of Abstracts*, 8th International Symposium on Biological and Environmental Reference Materials (BERM-8), September 17–22, Bethesda, MD, Abstract p. 110, "A New High Reliability Reference Material: Considerations of Synthetic Products"

(3) Ihnat, M. (2001) in *Reference Materials for Chemical Analysis-Certification, Availability, and Proper Usage*, M. Stoeppler, W.R. Wolf, & P.J. Jenks (Eds), Ch. 2.1, Wiley-VCH, Weinheim, Germany, pp 49–60

(4) Ihnat, M. (2001) in *Reference Materials for Chemical Analysis-Certification, Availability, and Proper Usage*, M. Stoeppler, W.R. Wolf, & P.J. Jenks (Eds), Ch. 2.1, Wiley-VCH, Weinheim, Germany, pp 20–30

(5) Ihnat, M. (Ed.) (2001) in *Reference Materials for Chemical Analysis-Certification, Availability, and Proper Usage*, M. Stoeppler, W.R. Wolf, & P.J. Jenks (Eds), Ch. 3, Wiley-VCH, Weinheim, Germany, pp 49–110

(6) Ihnat, M., Byrne, A.R., Kucera, J., & Quevauviller, P. (2001) in *Reference Materials for Chemical Analysis-Certification, Availability, and Proper Usage*, M. Stoeppler, W.R. Wolf, & P.J. Jenks (Eds), Ch. 3.2, Wiley-VCH, Weinheim, Germany, pp 101–110

(7) Ihnat, M., & Wolf, W.R. (2001) in *Reference Materials for Chemical Analysis-Certification, Availability, and Proper Usage*, M. Stoeppler, W.R. Wolf, & P.J. Jenks (Eds), Ch. 6.3, Wiley-VCH, Weinheim, Germany, pp 210–220

(8) Ihnat, M. (2001) *Fresenius' J. Anal. Chem*. **370**, 279–285

In connection with the Study Director's role as head of the Task Force on Multilaboratory Data Criteria for Reference Materials within the Technical Division on Reference Materials, he and the Task Force are assessing parameters to be specified in criteria for dealing with collaborative characterization of Reference and Control Materials. A progress report was presented at the Technical Division meeting at the 114th AOAC INTERNATIONAL Annual Meeting & Exposition, Philadelphia, PA, and a final report is intended to be delivered in the near future. Of relevance are the discussions underway at IAEA on a similar topic, in which the Study Director is a participant. He continues to play roles within the Technical Division on Reference Materials as liaison to the Methods Committee on Feeds, Fertilizers, and Agricultural Related Topics and is a member of the Reference Materials Methods Matching Committee.

Graphite Furnace Atomic Absorption Spectrometry: Method Advisor Robert W. Dabeka did not submit a report.

Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods: Study Director Nancy J. Miller-Ihli reported that there was no activity during the past year on this topic.

Graphite Furnace Atomic Absorption Spectrometric Determination of Lead in Sugar and Sugar Products: Study Director Nancy J. Miller-Ihli reported no additional progress on a simplified method for Pb in sugars.

Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Released from Ceramicware: Study Director Susan C. Hight reported no further activities on this topic following AOAC approval of the collaborative study. Papers describing development of the method and the collaborative study appeared as follows: Hight, S.C. (2001) *J. AOAC Int.* **84**, 861–872; Hight, S.C. (2000) *J. AOAC Int.* **83**, 1174–1188.

Lead in Calcium Supplements: No report was received from Study Director Paul H. Siitonen.

Lead in Wines: Study Director Alan L. Reisig reports that review of the collaborative study "Determination of Lead in Beverage Alcohol Using Graphite Furnace Atomic Absorption Spectrometry" is continuing to resolve some data treatment issues under discussion with the statistical advisor.

Neutron Activation Analysis: Study Director William C. Cunningham reported that there was no activity during the past year on neutron activation analysis as related to the AOAC endeavor.

Organometallics in Fish: This position is presently vacant. The current status of the recruitment of Method Advisor is being followed with AOAC.

Lead in Foods: Position vacant and proposal was made to merge it with the topic *Graphite Furnace Atomic Absorption Spectrometry* under Method Advisor Robert W. Dabeka.

Metals in Foods by Atomic Absorption Spectrometry: Method Advisor Lars Jorhem reported that 2 methods: **999.10** Lead, Cadmium, Zinc, Copper, and Iron in Foodstuffs, Atomic Absorption Spectrophotometry after Microwave Digestion; and **999.11** Determination of Metals in Foodstuffs, Atomic Absorption Spectrophotometry after Dry Ashing, appearing *Official Methods of Analysis,* 17th Ed., have been published as follows: Jorhem, L., & Engman, J. (2000) *J. AOAC Int.* **83**, 1189–1203; Jorhem, L. (2000) *J. AOAC Int.* **83**, 1204–1211.

Recommendations

(1) *Atomic Absorption Spectrometry*: Submit to *J. AOAC Int.* a report "*Flame Atomic Absorption Spectrometric Methodologies for Food Analysis—A Review*," comprehensively summarizing the status of current FAAS methods used by AOAC INTERNATIONAL and other agencies for major, minor, and trace elemental levels in foods and agricultural products. Use the proposals therein for consolidation of present AOAC official methods for individual and limited numbers of elements into a more unified scheme for multielement analysis of foods and related biological substrates. Complete development of a unified, comprehensive, multielement flame atomic absorption scheme of analysis of foods for a range of major, minor, and trace elements and submit next year for collaborative study approval and publication in *J. AOAC Int.* Complete a report for submission to *J. AOAC Int.* on the development and application of a highly reliable FAAS method for multielement determinations in biological materials. Continue study.

(2) *Graphite Furnace Atomic Absorption Spectrometry*: Continue study to resolve problems found for levels below 20 ppb Pb and 1 ppb Cd in the interlaboratory trial for the coprecipitation GFAAS method for these elements (*Can. J. Spectrosc.* **31**, 44–52[1986]); if problems are resolved, prepare a collaborative study protocol for approval by the General Referee, Committee Statistician, and Committee on Residues. Continue final validation study of graphite furnace method for total As and conduct an interlaboratory trial of an improved version of the coprecipitation GFAAS method (*Can. J. Spectrosc.* **30**, 154–157[1985]), or a solvent extraction method for As in foods. Continue study; review during coming year.

(3) *Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods*: Complete the collaborative study on the GFAAS method for the determination of Cr in foods and biological materials, based on the method published by the Study Director (*J. AOAC Int.* **75**, 354–359[1992]). Continue study.

(4) *Graphite Furnace Atomic Absorption Spectrometric Determination of Lead in Sugar and Sugar Products*: Consider for possible collaborative study, as an alternate method for Pb in sugars and sugar syrups, a simplified dissolution/GFAAS method (*At. Spectrosc.* **13**, 85–89[1994]). Continue study.

(5) *Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Released from Ceramicware*: Continue with study of shorter leach times.

(6) *Lead in Calcium Supplements*: Complete evaluation of the precollaborative trial based on the proposed collaborative study method, "Determination of Calcium by Inductively Coupled Plasma Atomic Emission Spectrometry and Lead by Graphite Furnace Atomic Absorption Spectrophotometry in Ca Supplements after Microwave Dissolution or Dry-Ash Digestion: Method Trial." Revise the collaborative study protocol to include the microwave dissolution procedure and prepare a protocol for collaborative study for approval by the General Referee, Committee Statistician, and Committee on Residues. Continue study.

(7) *Lead in Wines*: Complete revision of the collaborative study, "Lead in Beverage Alcohol, Graphite Furnace Atomic Absorption Spectrometric Method." Continue study.

(8) *Neutron Activation Analysis:* Evaluate the report on the interlaboratory study of method for the INAA determination of sodium in biological materials and begin processing toward official status. Continue study.

(9) *Organometallics in Fish:* Continue Official First Action status of the *Mercury (Methyl) in Seafood, Liquid Chromatographic–Atomic Absorption Spectrophotometric Method*, **990.04**. Appoint a new Study Director to continue work on this topic including completion of evaluation, as required, of the redesigned and simplified liquid chromatographic/AA interface and incorporate it into the method. Take the modified method through appropriate testing and approval procedures toward of-

APPENDIX

AOAC Study Director/Method Advisor List for Metals and Other Elements—Committee on Residues and Related Topics

General Referee

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Study Directors, Method Advisors

Atomic Absorption Spectrometry

MILAN IHNAT

Graphite Furnace Atomic Absorption Spectrometry

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Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods

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Graphite Furnace Atomic Absorption Spectrometric Determination of Lead in Sugar and Sugar Products

NANCY J. MILLER-IHLI

Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Released from Ceramicware

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Lead in Calcium Supplements

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Lead in Wines

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Metals in Foods by Atomic Absorption Spectrometry

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Neutron Activation Analysis

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nist.gov

Organometallics in Fish

VACANT

ficial status. Complete research into supercritical fluid extraction of methylmercury from seafood. If unsuccessful in getting new Associate Director, discontinue topic.

(10) *Lead in Foods*: Continue topic under the topic *Graphite Furnace Atomic Absorption Spectrometry*, under Method Advisor R.W. Dabeka. Continue study.

(11) *Metals in Foods by Atomic Absorption Spectrometry:* Continue study.

Multiclass Multiresidue Methods for Organic Compounds

CHARLES H. PARFITT
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Selected Topics

Pesticides in Nonfatty Foods Using SFE and GC/MS

Study Director Steven J. Lehotay, U.S. Department of Agriculture, has drafted and submitted for review, the final report for the collaborative study "Determination of Pesticide Residues in Nonfatty Foods by SFE and GC/MS." The study was conducted to determine multiple pesticide residues in apple, green bean, and carrot using supercritical fluid extraction (SPE) and gas chromatography/mass spectrometry.

Seventeen laboratories from 7 countries participated in the final study, and collaborators used a variety of different instruments. The procedure simply entails 3 steps: (*1*) Mix 1.1 g drying agent (Hydromatrix) per 1 g frozen portion of precomminuted sample and load 4–5.5 g of this mixed sample into a 7–10 mL extraction vessel; (*2*) perform SFE for 20–30 min with 1–2 mL/min flow rate of carbon dioxide at 0.85 g/mL density (320 atm, 60°C); and (*3*) inject the extract, which was collected on a solid-phase or liquid trap, into the GC/MS system, using either an ion trap in full scan mode or a quadrupole-type instrument in selected ion monitoring mode. The ability of GC/MS to simultaneously quantitate and confirm the identity of the semi-volatile analytes at trace concentrations is a strong feature of the approach. The selectivity of SFE and GC/MS avoids the need for post-extraction cleanup steps, and the conversion of the CO_2 solvent to a gas after SFE eliminates the solvent evaporation step common in traditional methods. The approach has several advantages, but its main drawback is the lower recoveries for the most polar analytes, such as methamidophos and acephate, and most nonpolars, such as pyrethroids.

Recoveries for the majority of pesticides are >75%, and nonpolars still achieve >50% recovery. The repeatability of recoveries within laboratories is generally <15% RSD. More specifically, the average results from 9 to 14 laboratories in the final analysis of 6 blind duplicates at 3 concentrations for each pesticide were as follows (*see* Table 1).

Table 1

Commodity	Pesticide	Spike conc. (ng/μL)	Recovery, %	Repeatability, %	Reproducibility, %
		Apples			
Carbofuran		75–500	89	7	9
Diazinon		60–400	83	13	17
Vinclozolin		6–400	97	13	18
Chlorpyrifos		50–300	104	10	12
Endosulfan Sulfate		150–1000	95	15	17
		Green bean			
Trifluralin		30–200	58	11	27
Dacthal		60–400	88	11	17
Quintozene		60–400	79	13	18
Chlorpyrifos		50–300	84	14	20
p,p′-DDE		45–300	64	14	27
		Carrot			
Atrazine		75–500	90	11	15
Metalaxyl		75–500	89	8	12
Parathion-me		75–500	84	14	15
Chlorpyrifos		50–300	77	13	19
Bifenthrin		90–600	63	12	25

All analytes except the nonpolars, trifluralin, p,p′-DDE, and bifenthrin, gave average Horwitz ratios <1.0 using AOAC criteria. The high repeatability and lower reproducibility of the 3 analytes that gave about 60% recovery, and general trend observed in results among laboratories, indicated that certain SFE instruments gave consistently lower recoveries for nonpolars than others. The collaborative study results demonstrate that the method meets the purpose for many monitoring programs for pesticide residue analysis, and the Study Director recommends that it be adopted Official First Action.

Miniaturized Methods

Topic Advisor Frank Schenck, FDA, Atlanta, GA, has evaluated the relative cleanup provided by 5 types of solid-phase (SPE) cartridges (aminopropyl, C18, graphitized carbon, primary secondary amine, and strong anion exchange) on acetone and acetonitrile extracts of fresh fruit and vegetables. The cleaned-up extracts were evaluated by gas chromatography with electron capture, flame photometric, and mass spectrometric detection. The aminopropyl and primary secondary amine cartridges provided the most effective cleanup, removing the greatest number of sample matrix interferences. The carbon cartridges removed most of the visible plant pigment in the extracts, but did little to eliminate matrix interferences "seen" by the detectors. Likewise, the C18 and SAX cartridges removed some plant pigment along with only minor amounts of sample matrix coextractant.

Comprehensive Multiresidue Methodology

Topic Advisor S. Mark Lee, California Dept. of Food & Agriculture, Sacramento, CA, reports that he is gathering data comparing conventional GC (FPD and ECD) analysis versus GC-MS and GC-AED with RTL. Qualitative results are good with MS/AED, which it screens against all known GC capable pesticides (almost 560+). Work remains to be done on comparison of quantitative results.

Recommendations

(1) **998.01** *Synthetic Pyrethroids:* Study Director Guo-Fang Pang, Qinhuangdao Entry-Exit and Quarantine Bureau, No. 39 Haibin Rd, PC 066002, Qinhuandao, People's Republic of China, Tel/Fax: +86-335-341-7119, E-mail: panggfciq@pang.com.cn. Method approved for First Action. Study Director reports that no work was conducted on this project during the last year. Prepare report on routine performance of **998.01** to support Final Action status for method.

(2) *Pesticides in Nonfatty Foods Using SFE and GC/MS:* Study Director Steven J. Lehotay, U.S. Department of Agriculture, Agricultural Research Service, Regional Research Center, Food Safety Research Unit, 600 East Mermaid Ln, Wyndmoor, PA 19038, Tel: +1-215-233-6433, Fax:

+1-215-233-6642, E-mail: slehotay@arserrc.gov. Complete review and submit the final report of the collaborative study to the Methods Committee for adoption.

(3) *Miniaturized Methods*: Topic Advisor Frank Schenck, FDA, Southeastern 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. Continue study.

(4) *Supercritical Fluid Extraction of Pesticide Residues in Foods*: Topic Advisor Marvin L. Hopper, FDA, Box 15905, Lenexa, KS 66285-5905, Tel: +1-913-752-2126, Fax: +1-913-752-2151, E-mail: mhopper@ora.fda.gov. Topic Advisor has suspended work on this project due to other agency research priorities. Prospects for returning to this project are very poor and the Topic Advisor has resigned. Eliminate this topic.

(5) *Comprehensive Multiresidue Methodology*: Topic Advisor S. Mark Lee, California Department of Food and Agriculture, Division of Inspection Services, 3292 Meadowview Rd, Sacramento, CA 95832, Tel: +1-916-262-1434, Fax: +1-916-262-1572, E-mail: mlee@cdfa.ca.gov. Continue study.

Single Class Multiresidue Methods for Organic Compounds

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Summary

This refereeship has covered a number of single class multiresidue method activities over the last year. These methods remain important where multiclass, multiresidue methods do not work or are not appropriate. Time has been spent discussing method work for dioxin, including a test kit for a dioxin receptor assay not discussed in this report. Dioxin discussions are still pending at this time. The General Referee has also discussed the Peer Verified Methods Program with several Study Directors. In addition, the scope and limits of this refereeship have been considered. The recommendations for the vacant topics are meant to start rationalizing this area. No new vacant topics have been advertised at this time but will be reviewed over the coming year.

Several references have been published recently that should be of interest to a residue chemist. One book is dedicated to the analysis of pesticide residues in food, *Pesticide Residues in Food*, 1999, John Wiley and Sons, by George Fong, Anson Moye, James Seiber, and John Toth. Wiley has also just published *Encyclopedia of Analytical Chemistry*, De 2000, edited by Robert Meyer. According to the prospectus, this reference work has about 20 chapters dedicated to residue analysis. One chapter, "Immunochemical Assays in Pesticide Analysis," posted on the Wiley Website, consists of about 16 pages of text, plus 11 pages of references, and includes a table of published antibodies. An *Encyclopedia of Separation Sciences* was published by Associated Press in August 2000, and edited by Ian Wilson et al. Information available via the Internet suggests that this reference also contains 4 articles on pesticide analysis, related to extraction, thin-layer chromatography, gas chromatography, and supercritical fluid chromatography techniques.

The *Pesticide Analytical Manual* (PAM), Volumes I and II, published by the U.S. Food and Drug Administration (FDA), in cooperation with the Environmental Protection Agency (EPA), is a good source of methods for pesticide residues in food. All of Volume I, which covers the broad multiclass, multiresidue methods, is on the FDA Website and was last updated in October 1999. The index to Volume II, which covers the single analyte pesticide methods within this refereeship, is also posted on the FDA Website. The Volume II index was last updated June 2000. The Web address for PAM is http://www.cfsan.fda.gov~lrd/pestadd.html. Methods can be obtained from FDA upon request.

EPA's Analytical Chemistry Laboratory Branch (ACL) also has posted an Index of Residue Analytical Methods on the EPA Website: http://www.epa.gov/oppbead1/methods. This Index contains all methods verified in ACL since 1980, including some methods not listed in PAM. Methods can be requested from ACL.

Although not an analytical chemistry reference, a 2 volume set entitled *Metabolic Pathways of Agrochemicals* published by the Royal Society of Chemistry in 1999, by Terry Roberts and David Hutson, is a valuable reference for anyone working with residue chemistry. These volumes contain individual monographs on the metabolism of each of a large number of agrochemicals. In a similar vein, Terry Roberts is also author of a textbook, *Metabolism of Agrochemicals in Plants*, J. Wiley and Sons, 2000. This latter book is more useful to provide a perspective on the plant metabolism of agrochemicals than as a source of metabolism data for individual pesticides.

Several reviews have been published. J. Sherma reviewed "Recent advances in thin-layer chromatography of pesticides" (1). And "Pesticide residue analysis: 1997–1998" (2). E. Hogendorn et al. reviewed "Recent and future developments of liquid chromatography in pesticide trace analysis" (3). A. Karcher et al. reviewed "Capillary electrophoresis and electrochromatography of pesticides and metabolites" (4).

Several papers reviewed use of immunoassays in food analysis, including pesticide detection. U. Schobel et al. reviewed "Immunoanalytical techniques for pesticide monitoring based on fluorescence detection" (5). J. Fitzpatrick reviewed "Applications and recent developments in the use of antibodies for analysis" (6). D. Hage et al. reviewed "Chromatographic immunoassays" (7). U. Bilitewski reviewed "Can affinity sensors be used to detect food contaminants?" (8). J. von Emon reviewed "Immunochemical applications in environmental science" (9).

Of the many papers that have been published over the last year on the analysis of pesticides, the following appear to be more interesting, or more novel than most, and are worth mentioning because they push new directions in pesticide residue analyses: K. Norman et al.: "Supercritical-fluid extraction and quantitative determination of organophosphorus pesticide residues in wheat and maize using

gas chromatography with flame photometric and mass spectrometric detection" (10). A flash GC method for organophosphates by K. Mastovska et al.: "Fast temperature programming in routine analysis of multiple pesticide residues in food matrixes" (11). P. Cooper et al.: "Capillary electrochromatography for pesticide analysis: effect of environmental matrixes" (12). J. Lipinski: "Automated multiple solid-phase microextraction: an approach to enhance the limit of detection for the determination of pesticides in water" (13). Z. Wang et al.: "Solid-phase microextraction coupled with liquid chromatography: a complimentary technique to solid-phase microextraction–gas chromatography for the analysis of pesticide residues in strawberries" (14).

Solid-phase microextraction (SPME) is becoming more common for pesticide analysis. A paper showing the applicability of SPME to nonvolatile pesticides was published by M. Sampedro et al. (15) entitled "Solid-phase microextraction for the determination of systemic and nonvolatile pesticides in river water using gas chromatography with nitrogen-phosphorus and electron-capture detection." A novel SPME approach using a molecular imprinted coating on the fiber was discussed in "Evaluation of a multidimensional solid-phase extraction platform for highly selective on-line cleanup and high-throughput LC–MS analysis of triazines in river water samples using molecularly imprinted polymers" by R. Koeber et al. (16). A novel approach, "Automated in-tube solid-phase microextraction–liquid chromatography for carbamate pesticide analysis" was described by Y. Gou et al. (17). Instead of dipping a solid fiber with an exterior coating into the sample as in regular SPME, in-tube SPME refers to sucking the sample into a short length of capillary tubing with its coating on the inside. Finally, R. Sasano et al. reported "Online coupling of solid-phase extraction to gas chromatography with fast solvent vaporization and concentration in an open injector liner" (18).

A paper entitled "Capillary electrophoresis microchips for separation and detection of organophosphate nerve agents," by A. Mulchandani et al. (19) presents an intriguing proposal for a hand-held analytical device. Rather than capillary electrophoresis, the separation technique is actually reported in the paper to be micellar electrokinetic chromatography, and detection is electrochemical. In another innovative electrochemical approach, A. Guiberteau-Cabanillas et al. have published "Study and determination of the pesticide imidacloprid by square wave adsorptive stripping voltammetry" (20).

S. Kunsagi-Mate et al. published "Host-guest interaction of calixarene molecules with natural benzotrifluorides: comparison of luminescence spectral data with results of model calculations relating to complex mixtures" (21). This paper suggests that calixarenes are promising host molecules to be used in chemical sensors for trifluoromethylbenzene related pesticides. J. King et al. published a paper (22), on "Solubility of triazine pesticides in pure and modified subcritical water." Although this is not a method paper, it provides preliminary information for potentially using a subcritical water extraction to determine triazines.

A number of papers on pesticide analysis were also published in *J. AOAC Int.* during this time frame. A guest editor section on pesticide residue analysis was published in *J. AOAC Int.* **83** in 2000, and another special section in *J. AOAC Int.* **84** in 2001 focused on immunoassay methods. Both contain a variety of useful information and methods.

Selected Associate Referee Topics

Polychlorinated Biphenyls in Blood

Method Advisor Virlyn Burse indicated that the method for which this topic was created was published in (23) and was accepted as Official Final Action in 1992. The topic was held open to accommodate a series of proposed modifications, including use of solid-phase extraction techniques to reduce solvent use. There has since been a switch to capillary gas chromatography to allow congener specific determination, and detection of PCBs is now routinely done using mass spectrometry with isotopic standards. Because the procedure has been so completely modernized, Method Advisor Burse believes it is no longer appropriate to consider modifications to the original procedure. Instead, the Method Advisor intends to initiate a new collaborative study of a new method for determining PCBs by capillary GC with mass spectrometric detection.

Phosphine in Cereal Grains

Method Advisor Kevin Norman reports that a description of this method was published in September 2000: Norman, K.N.T., & Leonard, K., "Gas chromatography–mass spectrometry determination of phosphine residues in stored products and processed foods" (24). Method Advisor Norman, however, has not been able to obtain funding for a collaborative study of this method. After carefully reading the requirements for a peer-verified method study of this procedure, Advisor Norman also does not believe that a peer verification can be supported. Therefore, Advisor Norman has recommended that this topic be discontinued.

Organonitro Compounds

Topic Advisor David Nortrup reports that all work has been discontinued on this topic. He recommends that the topic be discontinued.

Chlorinated Dioxins

Topic Advisor Douglas Hayward, FDA, reports renewed interest and activity in dioxin analysis at his agency. Topic Advisor Hayward has continuously been publishing papers on various aspects of the dioxin analysis. This year, following the work described in the Referee Report last year, he published a paper on "Quadrupole ion storage mass spectrometry and high resolution mass spectrometry: complimentary application in the measurement of 2,3,7,8-chlorine substituted dibenzo-*p*-dioxins and dibenzofurans in U.S. foods" (25).

The topic advisor also reports that participation in international studies indicates a major unresolved problem in standardizing how dioxin results are reported at, or near, the limit of detection. Laboratories vary in the sensitivities they can achieve in their dioxin analyses, and some may report real values at con-

centrations below the detection limit of other laboratories. Because of varying protocols for reporting results there is confusion about results that are reported as nondetects or trace findings, results that are actually nondetects but are instead reported by assigning the numerical value of the lower limit of detection, trace results that are reported by assigning the numerical value of the lower limit of quantitation, and real, measured results that are reported at very low levels using the most sensitive methods. This presents a major problem for interpretation by risk assessors attempting to use the integrated data.

The Topic Advisor also reports that he is implementing a greatly increased sampling program at his agency, including implementation of routine dioxin analysis at 2 additional laboratories besides his own. Testing of up to 2500 samples of a wide variety of both foods and feeds for dioxins, and possibly also for PCBs, is currently predicted. Topic Advisor Hayward is currently involved with harmonizing the different techniques available to these laboratories for dioxin analysis, developing a good set of reference materials, planning an analytical scheme that can address the variety of matrixes involved, and ensuring that all analysts are properly familiarized with the dioxin methodologies. This is very important in developing an AOAC Official collaborated method. Resolving these problems now will help ensure that the methodology and method instructions that are finally selected to become an Official method are rugged enough to be submitted to collaborative study. It will also help to identify critical control points in the methods and to generate the kinds of reference materials needed for distribution in a collaborative study.

Glyphosate

Study Director Phil Alferness has reported that the glyphosate method, **2000.05** "Determination of Glyphosate and (Aminomethyl) Phosphonic Acid in Crops by Capillary Gas Chromatography with a Mass Selective Detector," was approved as a First Action Official Method by the Official Methods Board in January 2000. Phil Alferness will continue as Study Director until the method is approved Final Action.

Triazine Residues in Raw Agricultural Products, GC Method

This topic is currently vacant. The General Referee notes, however, that all residues containing the chloro-triazine center have been expected to contribute to the same toxic endpoint for these compounds in food, and residues of the metabolites, especially diaminochlorotriazine, may predominate over residues of the parent triazines. Current multiresidue methods published by FDA in Volume I of the *Pesticide Analytical Manual* are capable of determining the parent triazines, but not simultaneously measuring all chloro-metabolites of these triazines. A method published by J.R. Pardue (26) and used in a brief survey of triazine residues detected the mono-desalkylmetabolites of simazine and atrazine, but required a second method to determine diaminochlorotriazine. A collaborated method capable of measuring all of these residues together seems highly desirable and the topic should be continued with this clarification.

Recommendations

(1) *Polychlorinated Biphenyls in Blood*: Topic Advisor Virlyn Burse, Centers for Disease Control and Prevention National Center for Environmental Health, 4125 Williamsburg Dr, College Park, GA 30337-4500, Tel: +1-770-488-4091, Fax: +1-770-488-4546, E-mail: vwb1@cdc.gov. Discontinue topic. Replace this topic with a new topic: Congener Specific Determination of PCBs by Capillary GC with Mass Spectrometric Detection.

(2) *Phosphine in Cereal Grains*: Method Advisor Kevin Norman, Central Science Laboratory, Sand Hutton, York, Y04-1LZ, United Kingdom, Tel: +44-(0)1904-462237, Fax: +44-(0)1904-462111, E-mail: k.norman@csl.gov.uk. Discontinue topic.

(3) *Organonitro Compounds*: Topic Advisor David Nortrup, U.S. Food and Drug Administration, 200 C St SW, Washington, DC 20204 Tel: +1-202-205-4390, Fax: +1-202-205-4422, E-mail: dnorthrup@cfsan.fda.gov. Discontinue topic. The Topic Advisor indicates that he has ceased all work on this topic.

(4) *Chlorinated Dioxins*: Topic Advisor Douglas Hayward, FDA, HFS 336, 200 C St SW, Washington, DC 20204, Tel: +1-202-205-4406, Fax: +1-202-205-4422, E-mail: douglas.hayward@cfsan.fda.gov. Continue topic.

(5) *Glyphosate*: Study Director Phil Alferness, Biomarin Pharmaceuticals, Inc., Ste 210, Analytical Biochemistry Department, 371 Bel Marin Keys Blvd, Novato, CA 94949 Tel: +1-415-506-6121, Fax: +1-415-382-0113, E-mail: palferness@biomarinpharm.com. Continue topic. The Study Director has agreed to stay on until the method is approved as Final Action.

(6) *Triazine Residues in Raw Agricultural Products,GC Method*: Vacant. Change topic to: Determination of Residues of Triazines and their Chloro-Metabolites in Raw Agricultural Commodities.

(7) *Substituted Ureas*: Vacant. Discontinue topic.

(8) *Dioxins by GC/MS*: Vacant. Continue topic. AOAC INTERNATIONAL has advertised for a Study Director for this topic and at least one tentative response has been received. The possibility of a collaborative study is currently being discussed. Pending further resolution, this topic should be continued.

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