

## METHODS COMMITTEE REPORTS

## Committee on Pesticide and Disinfectant Formulations

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### Committee Actions

The following activities are in progress: Packed column methods found in Chapter 7 of the *Official Methods of Analysis* are being updated by surveying manufacturers of the pesticide formulations in the chapter and regulatory laboratories. The information given, i.e., column type, film thickness, operating conditions, extraction solvents, etc., are being compiled. Information from the AAPCO check sample program is also being gathered and compiled. From this compilation of data, methods will come before the committee in order to determine if the changes are method extensions, minor, or major method. Method extensions will need a single-laboratory validation (SLV) to ensure the integrity of the changes. Minor changes will be decided on a case-by-case

basis to determine if an SLV will be needed for the changes. Major changes may need a full collaborative study.

A collaborative study protocol for the determination of phenols and phenates in ready-to-use and concentrate formulations is in progress and will be submitted to the committee by mid year.

The bifenthrin collaborative study has been approved to proceed to manuscript by unanimous vote of the committee. An applicability statement will be included in the draft of the collaborative study document.

### *Pesticide Formulations: Disinfectants*

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(1) *Quaternary Ammonium Compounds in Disinfectants, Automated Titration Method.*—A single-laboratory validation (SLV) study was conducted to determine the quaternary ammonium compounds (QAC) commonly found in disinfectants. AOAC does not have an official method for QAC determination other than the chloride titration procedure, which is not specific for QACs concerned because of possible chloride contribution from other sources.

Traditionally, QACs were analyzed using a biphasic (chloroform and water) manual titration procedure. Due to the safety considerations regarding chloroform, as well as the subjectiveness of color indicator-based manual titration determination, an automatic potentiometric titration procedure is proposed for quaternary nitrogen product formulations. Using the Metrohm Titrando system coupled with an ionic surfactant electrode and Ag/AgCl reference electrode, titrations were performed on various QAC-containing formulation products/matrixes with a standard sodium lauryl sulfate solution as titrant. The procedure appeared to be sufficiently reproducible and accurate for the purpose of regulatory product enforcement. The robustness of the method was measured by varying pH levels, as well as by comparing buffered versus unbuffered titration systems. Range of quantitation of 1–1000 ppm quaternary nitrogen was established. Eight commercially available formulated products covering a variety of matrixes were assayed, and results obtained were comparable to the traditional manual titration method. Spike recoveries between 94 and 104% were achieved. Recommendation is to proceed with a collaborative study. Continue topic.

(2) *Mixed Phenols and Phenates in Ready-to-Use and Concentrated Disinfectant Formulations.*—Disinfectant products containing mixed phenols/phenates comprise an important class of products used in hospital, institutional, and home settings. Analysis for the active ingredient(s) content of

these formulated products in support of the label claims and possible enforcement action requires reliable, rugged, validated analytical methods. AOAC Official Methods meet these requirements and provide an additional level of enforcement defensibility.

Existing analytical methods for disinfectant sample analyses currently in use include those from Environmental Protection Agency (EPA) and State Federal Insecticides, Fungicide, and Rodenticide (FIFRA) in-house files, EPA registration files, and industry/registrant files. Most of these methods have not achieved AOAC Official status through full collaborative testing/studies, but all have various degrees of validation by the respective laboratories. The methods currently in use are considered to be the best available and most suitable for the analyses of the specific products/samples for enforcement purposes. In many cases, these are the only methods available.

EPA's Analytical Chemistry Branch (ACB) and the Maryland Department of Agriculture State Chemist Section examined a liquid chromatographic (LC) and a gas chromatographic (GC) method currently in use for the analyses of phenol/phenate containing formulated products. The LC method was the method of choice for the Round Robin Study, and an in-house SLV was initiated and completed by Tom Phillips of the Maryland State Chemist Section. Six laboratories participated in the Round Robin Study; 4 Antimicrobial Testing Program laboratories plus 2 State FIFRA laboratories. Recommendation is to proceed with a collaborative study. Continue topic.

#### *CIPAC Studies*

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The 52nd Annual Meeting and Symposium of the Collaborative International Pesticide Analytical Council (CIPAC) was held June 9–17, 2008, in Braunschweig, Germany. The 7th Annual meetings of the Joint Meeting on Pesticide Specifications (JMPS) of the Food and Agriculture Organization (FAO) of the United Nations and World Health Organization (WHO) were held in conjunction with the CIPAC meeting and symposium. The meetings were held at the Federal Office of Consumer Protection and Food Safety (BVL). The BVL, which reports to the German Ministry, has authority for food safety and consumer protection in Germany and works in cooperation with the European Commission in the area of risk communication.

Welcoming remarks, thanks for attendance and participation, plus continuing support were expressed for all meetings during the general opening session by Ralf Hanel, Chairman of CIPAC and organizer of the meetings, Yong Zhen Yang, FAO Joint Secretary of the JMPS, Morteza Zaim,

Manager of the WHO Pesticide Evaluation Scheme (WHOPES), and Dennis Hamilton, JMPS Chairman. Hanel and Yang extended noted welcomes to Helmut Tschiersky-Schoneburg, Head of the Federal Office of Consumer Protection and Safety (BVL), Karola Schorn, Head of Unit 517 Plant Protection at the Federal Ministry of Food, Agriculture and Consumer Protection, and Hans-Gerd Nolting, Head of the Department of Plant Protection at BVL.

Yang noted that this was the 5th time the CIPAC meeting was held in Braunschweig and anticipates continued activities and cooperation between and among the BVL, FAO/WHO JMPS, and CIPAC. She expects the collaboration will continue among the partner organizations in regard to pesticide specifications and quality.

Yang provided an update of the status of publication of the specifications for the FAO list of pesticide compounds from 2002 to 2007, including an update to May. There are 17 pesticide compounds remaining on the list. She also provided a list of pesticide compounds for withdrawal of FAO specifications developed under the old procedure. Methods for impurities in these compounds are not included and the specifications are no longer supported by industry.

Zaim provided a priority list and program for development of FAO and WHO specifications for pesticides for the JMPS in 2009. The priority lists the pesticides in 3 categories: (1) original proposer; (2) subsequent proposer; and (3) specification for formulation.

The absence of Gero Vaagt (FAO), who previously served as the Joint Secretary of JMPS, was duly noted at the meeting as he has accepted a new position in Nicaragua. His contributions to the JMPS and meetings were warmly acknowledged.

The Acting General Referee for CIPAC Studies provided a presentation for the joint open meeting, *Technical Liaison with Other Organizations—AOAC INTERNATIONAL*, which Hanel read into the minutes.

A brief summary of CIPAC actions taken after last year's meeting include a systematic review of CIPAC methods in order to publish Handbook M in the latter half of 2009; the development of guidelines for independent laboratory validations of methods for relevant impurities; development of a systematic review process and prepublication scheme for CIPAC methods; and ongoing administrative processes and functions. It was noted (with a presentation by Markus Muller and Laszlo Bura) that CIPAC has been publishing methods books since 1980 and manuals before that. Many methods, as in Chapter 7 of the OMA, utilize outdated technology and are themselves outdated. CIPAC, as mentioned above, initiated a systematic review of these methods beginning with the oldest in Handbook "E." The obsolete methods will be listed and no longer supported. No method extensions will be granted for obsolete methods, but they may be used in special instances or situations.

The collaborative studies conducted during the year were presented and discussed. A review of methods resulted in the following actions: 6 analytical methods were accepted as provisional CIPAC methods, while 3 remain provisional;

6 analytical methods were accepted as full CIPAC methods; one analytical method extension was accepted as provisional, and 4 were accepted as full CIPAC methods; and 2 analytical methods remain tentative. A reversed-phase LC method for clothiadin in technical materials and water dispersible granules formulations was recommended for a full collaborative study. The independent laboratory-validated LC-UV method for the determination of the *N*-nitroso relevant impurity in pendimethalin technical material and emusifiable concentrate was noticed and regarded to be suitable for such determinations.

*Recommendations*

- (1) Continue involvement with CIPAC.
- (2) Encourage participation in upcoming CIPAC collaborative studies.
- (3) Consider adoption and application of CIPAC's review process of older methods to the review of OMA Chapter 7.
- (4) Bring forward collaborated CIPAC for inclusion and adoption as AOAC Methods in OMA Chapter 7.

*Pesticide Formulations: Insecticides*

Vacant

*Pesticide Formulations: Herbicides*

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No report filed.

*Pesticide Formulations: Fungicides and Rodenticides*

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No report filed.