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Committee on Pesticides and Disinfectant Formulations

Pesticide Formulations: CIPAC Methods

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Summary

The 46th Annual Meeting and Symposium of the Collaborative International Pesticide Analytical Council (CIPAC) was held during mid-June in Rome, Italy. Immediately before and in conjunction with the CIPAC meeting and symposium, the first joint meetings on pesticide specifications (JMPS) of the Food and Agriculture (FAO) and World Health Organizations (WHO) were held, including open and closed formal sessions. All meeting sessions were at the FAO Headquarters (Rome, Italy) while the symposium was organized and held at the Istituto Superiore di Sanita, the main Italian institution of scientific-technical research, control, and advice in public health. The meetings were organized by local hosts Gero Vaagt (Senior Officer, Pesticide Management Group, Plant Production and Protection Division, FAO, 00100 Rome, Italy) and Roberto Dommarco (Laboratorio di Tossicologia Applicata Istituto Superiore di Sanita, Rome, Italy), who were also responsible for the exceptional arrangements of the meetings and associated events. Warm welcome to the meeting with support and encouragement for the work at hand were delivered at the opening session by M. Solh (Director Plant Production and Protection, FAO), Maria Neira (Director Communicable Disease Control, Prevention and Eradication, WHO), R. Marbelle (Italian Ministry of Health), and Water Dobrat (Chairman, CIPAC).

As establishment of pesticide specifications under the new procedure of FAO entered its 4th year of operation, a significant change, which has been in actual development for a few years, was made to incorporate WHO pesticide specifications as well. While WHO has been establishing pesticide specification for public health pesticides for several years, working together with FAO provides each organization with efficiencies and a common base. In order to create what is now called JMPS, very significant efforts were made by M. Zaim (WHO Pesticide Evaluation Scheme, WHO, Avenue Appia, CH1211 Geneva 27 Switzerland), Gero Vaagt (FAO) and A.R.C. Hill (Central Science Laboratory, Sand Hutton, York, YO4 1LZ, UK) along with support and input from those who are members of JMPS and representatives of pesticide producers. An important product of these efforts will be the 1st Ed. of the *Manual on Development and Use of FAO and WHO Specifications for Pesticides*. Changes in the manual resulting from

comments on the May 2002 draft plus changes covering household pesticides and microbial larvicides will be incorporated. Likely the new manual will be available at the end of the year, in time for use by JMPS in 2003, and may be downloaded from the FAO Pesticide Management Web site at <http://www.fao.org/ag/AGP/AGPP/Pesticid/Default.htm>.

A number of actions since the last meetings on pesticide specifications (the 31st meeting, 2001) were reviewed at the JMPS open session:

(1) *International Code of Conduct on the Distribution and Use of Pesticides*.—Protection of property rights has been an important concern during revision of the code. Where JMPS is involved, language in the new manual and the declaration of interest requirements of JMPS panel members appears in line with industries' need for confidentiality.

(2) *Joint FAO/WHO Meeting on Pesticide Residues (JMPS) and the Codex Committee on Pesticide Residues (CCPR)*.—As reported last year, JMPS and CCPR are looking to link with JMPS as an early first step into their processes of developing maximum residue levels used in world trade of food. The number of reviews that need to be done by JMPS and CCPR presents a nearly unmanageable challenge which in turn challenges JMPS in its work on pesticide specifications. JMPS, JMPS, and CCPR would like to begin this coordinated linkage by 2003 to provide JMPS specifications on those pesticides they will consider in 2004. This will begin as a voluntary effort, but it needs advance plans of work if it is not to slow the development of pesticide standards for trade. The path to such standards begins with validated methods for pesticide products (technical and formulated).

(3) *Review of Old Specifications*.—The specifications applicable for the JMPS/CCPR work on standards for pesticide residues are only those being developed under the new procedure begun in 1999. In the review of specifications that need consideration under the new process, some old specifications will be proposed for withdrawal where the pesticides are no longer in use, have been identified as persistent organic pollutants, or have been discontinued or banned due to health problems.

(4) *Roster Call for JMPS*.—With the demand for specifications growing, more JMPS experts are needed. There is a call for candidates on the FAO Web site for specifications (<http://www.fao.org/WAICENT/FAOINFO/AGRICULT/AGP/AGPP/Pesticid>). Requirements for those who serve on JMPS are given at the site. So far at least 60 applications have been submitted.

(5) *JMPS Manual*.—It is mentioned above that revision of the manual on the new procedure will likely be published this year, and is available as indicated at the FAO Web site. There will be additional specification guidelines to be added. Other additions to the new procedure will include a letter of authorization by the proposer to allow JMPS experts (evaluators) to

see data on file at a registration authority or request the registration authority to provide feedback in comparison of data submitted to JMPS and registration data on file; identification by the proposer of links, if any, between relevant impurities and submitted ecotoxicological and toxicological data; attachment of methods by proposers for methods that are not AOAC or CIPAC; and WHO recommendations on efficacy may be used where such exists to support specifications.

Again this year, specifications proposed as new, revised from old specifications, carried over from prior reviews or additions to existing, new procedure specification were considered in Rome. Records of the reviews were made by J. Gillespie (UK Pesticide Safety Directorate, York, UK) and A. Kouppari (Department of Agriculture, Pesticide Laboratories, Nicosia, Cyprus), while guidance and leadership were provided by A.R.C. Hill (Chairman, JMPS), Gero Vaagt (FAO), and M. Zimme (WHO), with industry leadership input by Thomas S. Woods (Crop Life International/DuPont). Approvals from the Rome meetings will be individually posted as finalized on the FAO Worldwide Web pages of <http://www.fao.org/Waicent/FAOINFO/AGRICULT/AGP/AGPP/Pesticide> and by WHO where applicable at <http://www.who.int/ctd/whopes/specificationsandmethods.htm>. The FAO site currently has 14 postings of new procedure specifications, 4 of which are from 2001.

An important general principle related to pesticide specifications and the chemical methods for product active ingredient identification received significant discussion and emphasis as numerous isomer specific pesticides were reviewed. While isomer specific analytical methods are most desirable, such may not always be practical; however, as a starting and receiving point check for goods in trade, isomer specific identity tests have great significance in relation to product quality, potential environmental impact, and surely to value for funds expended. Thus, adequate emphasis was given and should be expected for the future, where applicable, on the specificity of identity test in CIPAC methods and pesticide specification review by JMPS.

The CIPAC Symposium was held after the JMPS, but before the CIPAC technical meetings. Approximately 80 scientists from around the world were in attendance. This year the symposium consisted of 10 papers on regulatory, environmental, and analytical topics including: European Union pesticide legislation, the WHO pesticide evaluation scheme, chiral stability of pesticides in the environment, near infrared spectroscopy and capillary electrophoreses applications in pesticide analysis, and measurement of release properties of microencapsulated pesticides. Determination of the distribution of active ingredient between that which is free and that which is encapsulated is of great importance, although usually quite under appreciated. Whether encapsulated for the purpose of improved user safety, time extended effectiveness or obtaining efficacy at lower rates of application/less frequent application, integrity and content of the encapsulated portion of active ingredient can be a significant element of product quality. A.R.C. Hill and D.J. Hamilton (Animal and Plant Health Service, Department of Primary Industries, Brisbane,

Australia) were co-moderators of the Symposium sessions, with D. J. Hamilton concluding the day with a summary of the program.

The 2 days of CIPAC technical sessions were both busy and well organized by the CIPAC Secretary, M.D. Müller (Swiss Federal Research Station, CH-8820 Wädenswil, Switzerland), in his first and only year for this role as he is assuming the reins of CIPAC as Chairman this year. The new CIPAC Secretary is L. Bura (Plant Health and Soil Protection Station, PF 340, Budaörsi ut 141, 1118 Budapest, Hungary). From review of the methods and studies presented at the meeting, the following actions were taken: 5 analytical methods were accepted as provisional CIPAC methods as was one method extension; 4 previously accepted provisional analytical methods were accepted as full CIPAC methods, as were 4 method extensions; and 2 physical test methods were accepted as provisional. These method actions were made under the fine leadership of retiring CIPAC Chairman, Walter Dobrat, who served as CIPAC Assistant Secretary for several years, making significant contributions on editorial efforts for CIPAC Handbooks. Dobrat was succeeded by Joe Gillespie as Assistant Secretary in 2000, who is succeeded by Ana Kouppori this year. CIPAC will miss Dobrat and Gillespie, while entering a new year with an entirely new group of officers, including the treasurer, Bryan E. Hocken, who replaced M.J.P. Harrington at the close of the 2001 meeting in Bangkok.

During the CIPAC management meeting, it was agreed to revise its cooperative agreement with AOAC. Similarly, under consideration is a like agreement on physical methods with ASTM.

Four small scale or preliminary analytical studies, which will very likely be the subject of full collaborative studies this year, were reported at the CIPAC meeting: d-allethrin, parathion-methyl, d-phenothrin, and prallethrin. Laboratories who are interested in receiving notice of these and other CIPAC studies, but not routinely receiving CIPAC study information sheets, should notify this General Referee and be placed on the list of laboratories to be provided announcements of CIPAC studies. Twenty-two pesticide product methods and 9 MT or physical methods have recently been published in CIPAC Handbook J. Information needed for ordering CIPAC handbooks is available on the CIPAC home page (<http://www.cipac.org>, click on "CIPAC Publications").

Selected Topics

CIPAC Provisional Methods

Cycloxydim (Selective Postemergence Grass Herbicide, a Graminicide): Nineteen of 21 laboratories, representing 12 countries, returned data after analysis of 5 samples representing 5 materials: 3 emulsifiable concentrates (EC), one technical concentrate (TK), and one technical material (TC). Analyses were performed using an LC phenyl column with detection at 280 nm and electronic integrator or data system plus external standardization. One outlier result was found in statistical evaluation of the data from analysis of each of 4 of

the 5 test samples. Except for one of the test samples, method performance was quite acceptable without outlier removal. This German PAC study was directed by R. Eisert and G. Genari, both of BASF (Agricultural Center Limburgerhof, Crop Protection Development, PO Box 120, D-67114 Limburgerhof, Germany), with presentation by G. Genari.

Esfenvalerate (Broad Spectrum Insecticide): After a successful small scale study reported at the 45th CIPAC meeting, Ritsuko Furuta (Sumitomo Chemical Co., Ltd., Environmental Health Science Laboratory, 3-1-98, Kasugade-naka, Konohanaku, Osaka, Japan) directed and presented a full collaborative under the Japanese PAC. Capillary GC was used to separate esfenvalerate, the *S,S* and *R,R* isomers in one peak, separate from the *R,S* and *S,R* isomers, for detection by FID and area integration by electronic integrator or data system. Of the 12 laboratories, located in 8 countries, participating and returning data sets, 2 were found to have consistently produced

outlier results on the 5 test samples analyzed of 5 materials: 2 of technical concentrates (TK) and 3 of ultra low volume (UL) formulations. Method performance was acceptable for the TC test samples without removal of outliers, but considerably improved after removal, while performance was only marginally acceptable for one UL and unacceptable for one before removal of outliers. Method performance was acceptable for all UL formulations after outlier removal.

This study also included an LC normal-phase method for determination of the *R,R* isomer of esfenvalerate as a percentage of the *R,R* and *S,S* total, which was consistently around 1% of the combined GC peak of *R,R* and *S,S* isomers; however, the relative standard deviations were rather high, as might be somewhat accounted for and expected at such a low level. The LC method does provide confirmation of identity relative to expected *R,R* and *S,S* isomer composition.

Table 1. Summary of decisions made at the 46th CIPAC meeting

Code No.	Name	Status
12	Malathion	The capillary GC method for malathion and formulations (TC, EC, EW, DP), CIPAC/4267R, has been accepted as provisional.
171	Oxydemeton-methyl	The LC provisional method for oxydemeton-methyl and formulations (TC, EC, SL), CIPAC/4247, has been accepted as full.
221	Chlorpyrifos	The extension of the AOAC-CIPAC LC method for chlorpyrifos to ultra low volume formulations (UL), CIPAC IC, has been accepted provisional.
391	Chlorsulfuron	The extension of the CIPAC LC method for chlorsulfuron to wettable powders (WP), CIPAC H, p89 (CIPAC/4257), has been made full.
441	Metsulfuron-methyl	The extension of the CIPAC LC method for metsulfuron-methyl wettable powders (WP), CIPAC H, p205 (CIPAC/4256), has been made full.
471	Etofenprox	The capillary GC method for etofenprox technical and formulations (WP, EC, OW), CIPAC/4239, has been made full.
481	Esfinvalerate	The capillary GC and the LC method for esfinvalerate technical and formulations (UL), CIPAC/4269, have been made provisional.
502	Bensulfuron-methyl	The extension of the CIPAC LC method to bensulfuron-methyl wettable powders (WP), CIPAC/4258, has been made full.
510	Cycloxydim	The LC method for cycloxydim technical and formulations (TK, EC), CIPAC/4287, has been made provisional.
546	Tribenuron-methyl	The LC method for tribenuron-methyl technical and formulations (DF, WG), CIPAC/4283, has been made provisional.
568	Kresoxim-methyl	The LC provisional method for kresoxim-methyl technical and formulations (WG, SC, SE), CIPAC/4250, has been made full.
582	Imidacloprid	The LC method for imidacloprid FS formulation, CIPAC/4253, has been made full.
599	Nicosamide	The extension of the CIPAC LC method for nicosamide formulation suspension concentrate (SC), CIPAC/4252, has been made full.
740	Icaridin	The LC method for icaridin technical and formulation (lotion), CIPAC/4248, has been made provisional.
741	transfluthrin	The capillary GC method for tranfluthrin technical and formulation (lotion), CIPAC/4239, has been made provisional.
MT 187	Particle size analysis by laser diffraction	The method for determination of particle size by laser diffraction of pesticide formulations (WP, WG, SC), CIPAC/4279, has been made provisional.
MT 178	Attrition resistance	The method for determination of attrition resistance of granules, CIPAC/4280, has been made provisional.

Icaridin (Repellent): Sixteen laboratories from 9 countries volunteered for this study and 13 returned data sets on 2 technical materials (TC) and 3 lotion formulations. Analyses were performed using capillary GC for separation, flame ionization for detection and peak area ratio determination with the internal standard using an electronic integration or data system. No result was removed for either TC and only 4 results were removed for the 3 lotions analyzed after statistical evaluation of all data sets. Method performance was excellent for the TC products and adequate for the lotion formulations in this study directed under the German PAC and presented at CIPAC by T. Werner (Bayer AG, ZF-ZAD, Postfach 100140, D-41538 Dormagen, Germany).

Malathion (Insecticide): One technical material (TC), one emulsifiable concentrate (EC), 2 oil in water emulsions (EW), and one dustable powder (DP) were analyzed by separation on capillary GC, flame ionization detection, internal standard peak area ratios, with electronic integrator or data system integration of peak areas for quantitation. Twenty-three laboratories representing 19 countries returned data sets. Statistical

analysis identified only 2 results from one laboratory that were removed as outliers. Method performance was satisfactory for all materials analyzed in this study directed by Elsa V. Sorensen (Cheminova A/S, PO Box 9, DK-7620 Lemvig, Denmark), who also presented the results at CIPAC.

Tribenuron-methyl (Broadleaf Herbicide): No fewer than 19 results remained for each material after outlier removal from statistical analysis of the data returned by 23 laboratories from 14 countries. Analysis of 2 technical materials (TC), 2 dry flowables (DF), and 2 water dispersible granules (WG) was conducted using LC-reversed-phase chromatography with internal standard, detection at 254 nm and peak area determination with electronic integration or data system. Good method performance was found for all test samples analyzed in this study directed and presented by David E. Brennan (DuPont Crop Protection, Stine-Haskell Research Center, PO Box 30, Newark, DE 19714-0030, USA).

Recommendations

None.