CIPAC STATUS REPORT

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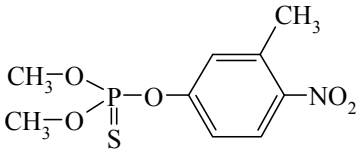

0035 Fenitrothion

Allocated to WHO

CIPAC methods published in:

CIPAC 1A, p. 1255 (titr.)
CIPAC 1C, p. 2119 (GLC)

CIPAC 14th meeting, June 1970 in Gembloux

Decision The committee will wait for the results of the WHO trial, but it is recommended to continue in the meantime with the work, in order to avoid the use of pure fenitrothion as standard and to delete, if possible, the correction factor for incomplete hydrolysis.

CIPAC 15th meeting, October 1971 in Washington

Decision The WHO method IS/1.00433 is adopted as provisional WHOCIPAC method, supported by the collaborative work carried out by WHO. However, as the method is not specific, an identification test should be needful.

CIPAC 17th meeting, June 1973 in Wageningen

Decision It was agreed to combine the WHOCIPAC method with method 1385 for free 3methyl4nitrophenol and easily hydrolysable impurities, to be published in 1A.

CIPAC 24th meeting, May 1980 in Salobrena

Mr Quélennec reported that the WHO had a GLC method, which had not been tested collaboratively.

CIPAC 27th meeting, July 1983 in Brisbane

Decision. The GLC method for fenitrothion technical and formulations, presented at the symposium by Mr Miles was adopted as provisional WHOCIPAC method (published in 1C).

CIPAC 33rd meeting, May 1989 in Lagonissi

There is a firstaction AOAC method by GLC for WG's and EC's but CIPAC would stick to its own method.

CIPAC 36th meeting, October 1992 in Zurich

The official final action GLC method had been superseded by a superior GLC method.

CIPAC 51st meeting, June 2007 in Umhlanga Rocks, South Africa

As a replacement for the obsolete packed column GC method, Mr Asada presented the results of a small-scale collaborative trial on the determination of fenitrothion in a TC, a WP, two EC, and 2 UL formulations, using normal phase HPLC, a CN column, UV detection at 268 nm, and external standardisation.
The column used was 250 × 4.6 (i.d.) mm, stainless steel, packed with Zorbax CN (5µm), or equivalent. Questions were about the use of hexane and whether it was possible to replace this toxic solvent by heptane. The identity test proposed was based on the IR spectrum with a KBr pellet and the replacement with a liquid film on NaCl was suggested.
Six laboratories participated in the trial. For all samples, the values of RSD_R (reproducibility relative standard deviation) were smaller than those calculated by Horwitz's equation. The proposed method is considered appropriate for the determination of fenitrothion in TC, WP, EC and UL formulations, and it was proposed that the study go to a full collaborative study.

CIPAC 52nd meeting, June 2008 in Braunschweig

Mr Yasushi Asada presented the results of a small-scale collaborative study by JAPAC on the determination of fenitrothion in the TC, WP, EC and UL, by normal phase HPLC using a CN column, UV detection at 268 nm and external standardisation.
Samples were sent to 15 laboratories and 14 returned results. The 15th laboratory informed the organizer that it would not be able to perform the trial due to the participant undergoing surgery prior to the trial. Detailed statistical evaluations were shown and discussed. Statistical evaluations were carried out according to ISO 5725.
The values of RSD_R for all samples were smaller than those calculated by the Horwitz equation.
The proposed method is considered appropriate for the determination of fenitrothion in the technical product, wettable powder, emulsifiable concentrate, and ultra-low volume liquid. JAPAC proposed that the HPLC method be accepted as a provisional CIPAC method.
Decision The normal phase HPLC method (CIPAC/4602) for the determination of fenitrothion in TC, WP, EC and UL formulations was accepted as **provisional** CIPAC method, It was agreed to remove the results of laboratory 5 from the statistical evaluation.

CIPAC 53rd meeting, June 2009 in Sonsonate/El Salvador

The normal phase HPLC method (CIPAC/4602) for the determination of fenitrothion in TC, WP, EC and UL formulations was accepted as a **full** CIPAC method. (the results of laboratory 5 was removed from the statistical evaluation)

***S*-methyl-fenitrothion in fenitrothion** (Imp 7, Imp12)

CIPAC 28th meeting, October 1984 in Baltimore

Dr Beckmann presented results of the determination of S-methyl fenitrothion in several samples (CIPAC/3222). GLC and HPLC methods had been used and had given comparable results. The HPLC method was preferred because of its rapidity. The Joint FAO-WHO Meeting should cover the toxicological aspects and decide whether or not the amount should be limited.
Dr Adam will take up with the Joint Meeting. The oxon analogue had not been determined.

CIPAC 32nd meeting, June 1988 in Geneva

Although there was a clause in the FAO specification for the S-methyl isomer, a collaborative studied method might not be necessary; a method supplied by the manufacturer(s) might be sufficient.

CIPAC B35th meeting, June 1991 in Braunschweig_D

For FAO and WHO specifications a method was needed. Mr Sakaue seemed to have supplied a HPLC method some years ago, which Mr Thomsen promised to supply. It was remarked that a short inert capillary column might also work.

CIPAC 51st meeting, June 2007 in Umhlanga Rocks, South Africa

S-methyl fenitrothion is considered to be a relevant impurity in fenitrothion TC and in formulations. A peer validation was undertaken and the results presented.
The peer validation was performed as follows based on consultation with CIPAC:
1) validate the analytical method in terms of specificity, linearity, accuracy, quantitation limit and repeatability in one laboratory.
2) validate the analytical method in terms of reproducibility by analyzing the same samples in two independent laboratories (one of the laboratories is the laboratory above). 6 labs participating. Fenitrothion technical (TC), wettable powder (WP), emulsifiable concentrate (EC-1, EC-2), ultra-low volume liquid (UL-1, UL-2)
The same analytical conditions as for fenitrothion content are used. The sample preparation is the same as for the content in TC and in formulations. With the chromatographic conditions used, S-methyl fenitrothion is well separated from fenitrothion and was shown to be essentially free from interfering signals.
For all samples, the analytical method was validated in terms of specificity, linearity, accuracy, quantitation limit and repeatability. Reproducibility was confirmed by analysing the samples in two independent laboratories. In conclusion, the proposed method was successfully peer validated and was considered appropriate for the determination of *S*-methyl fenitrothion in technical material, wettable powder, emulsifiable concentrate and ultra-low volume liquid. The recommendation was to adopt the method as CIPAC method for the determination of S-methyl-fenitrothion in fenitrothion.
Comments were, that hexane is a useful but toxic solvent and should be exchanged for heptane wherever possible.

TMPP in fenitrothion

CIPAC 53rd meeting, June 2009 in Sonsonate/El Salvador

Mr Yasushi Asada presented the results of the peer validation for the determination of the tetramethyl pyrophosphorothioate (TMPP) content in fenitrothion TC, WP, EC, and UL formulations, using capillary GC–FID and internal standardisation (*n*-butyl benzoate). The peer validation was conducted with four independent laboratories through the network of JAPAC.
For all samples, the analytical method was peer-validated in terms of specificity, linearity, repeatability and LOQ. The RSDs of repeatability for the TC and all formulations were found to be less than 20% for all laboratories that participated in this peer validation. The proposed method was successfully peer-validated and was considered appropriate for the determination of TMPP in fenitrothion TC, WP, EC and UL formulations.
Decision: The capillary GC method for the determination of the relevant impurity TMPP in fenithrothion TC, WP, EC and UL formulations (CIPAC/4660) was noticed and adopted.