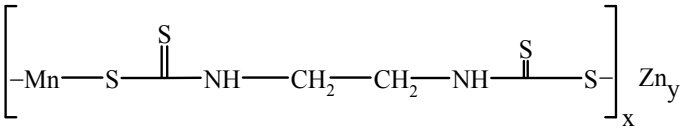
CIPAC STATUS REPORT

16/09/2020



0034 Mancozeb

Allocated to G.B.

CIPAC methods published in :

CIPAC 1A, p. 1288 (titr.)
H, p. 96 (+ Cu)

CIPAC 15th meeting, October 1971 in Washington

Decision The method 1712, supported by report 1711, for the determination of Zn and Mn is accepted as full CIPAC method. The method 1709, supported by report 1710, for the determination of the pH in the suspensions is accepted as full CIPAC method.

CIPAC 16th meeting, June 1972 in Stockholm

Decision The CS_2 evolution methods for technical (1868), dusts (1869) and dispersible powders (1870), supported by the report 1871, are adopted as full CIPAC methods. Rohm & Haas Co. has presented some objections about the conditions of analysis, but not supported by a report. The Committee is waiting for such a report on the influence of acidity and of reaction time.

CIPAC 17th meeting, June 1973 in Wageningen

Decision The colorimetric method for distinguishing between mancozeb and other dithiocarbamate compounds, as presented by the Dithiocarbamate Subcommittee, is adopted as provisional method if the final report is available in time for 1A, but as draft method if the report is not available.

CIPAC 18th meeting, June 1974 in London

Decision Identity test hoped satisfactory. Dubosq method (with hydroiodic acid) for mancozeb is adopted as provisional method for inclusion an 1A.

CIPAC 26th meeting, May 1981 in Rome

Mr Schoeni presented an additional identification test at the symposium. It was essential now the patents were running out to distinguish mancozeb from other complexes. The dithizone test was to difficult to carry out. Mr Lovett remarked that the whole procedure had to be followed. One should not pick out hits of the test. He agreed that mancozeb prepared from different Zn salts would give different reactions.

CIPAC 28th meeting, October 1984 in Baltimore

A collaborative survey had been held with 4 identification methods (CIPAC/3158). The results of the UV and Riasetto tests were difficult to interpretate. The MT 130 method had given no false positives. The study would be repeated with a new set of fresh samples. Mr Henriet drew attention to his proposal for identifying dithiocarbamates using a dichotomic system. Mr Beckmann reported recovery difficulties in mancozeb samples that contained sulphur (CIPAC/3213). Mr Stevenson suggested that it might be matter of poor wetting.

CIPAC STATUS REPORT

16/09/2020

CIPAC 29th meeting, September 1985 in Copenhagen

The report (CIPAC/3243) of the collaborative study with modified dithizone (CIPAC/3244) and UV tests (CIPAC/3245) were presented by Mr Stevenson (see also DITH report CIPAC/3234). The Riasetto test and the CHBr_T3_H test had not been investigated further. It was understood that the UV method was a support method. The dithizone method did not work with SC formulations nor could it be used with coloured products. It was important to use the right reagents e.g. CHCl_T3_H without EtOH (Re 64). The particle size might also influence the reaction.
Decision . The modified identity test method MT 130 (CIPAC/3244) was accepted as full CIPAC method (not applicable to SC's and coloured formulations). The UV absorption test for evaluation of ethylenebisdithiocarbamates (CIPAC/3245) was accepted as full CIPAC method (MT 165).

CIPAC 45th meeting, June 2001 in Bangkok

Aventis was considering a HPLC method (see 4223). Mr Hill drew attention to the need for a proper identity test.

CIPAC 60th meeting, June 2016 in Tokyo

Mancozeb by Ms Bu Haiyan (5047, 5048)
Ms Haiyan presented the results of a small scale collaborative study with 5 laboratories on an HPLC-UV method for analysing mancozeb in technical and WP formulations. The concentrations of mancozeb in the sample solutions were determined by external calibration method. The mobile phase and the diluted sample solution should be kept under alkaline conditions, pH 9.5-10.0, to avoid decomposition of the mancozeb. The linearity, selectivity, recovery and repeatability of the proposed method were evaluated. Comparison of the results using existing CIPAC method and the proposed HPLC method gave good results, differences less than 1%. The statistical evaluation of data was carried out according to ISO 5725 guidelines. Three results were identified as outlier (Grubbs test and Cochran variance homogeneity test). It was assumed that incomplete dissolution of the sample was responsible for these outlier and stragglers.
The RSD_R as determined from the collaborative study is not larger than RSD_R (calc.). Based on the results of this study, it was proposed to perform a CIPAC collaborative study to determine mancozeb in TC and WP by the HPLC method.
The following comments were received from the meeting:

- Was there any reason to use for column temperature 29 °C? The answer was that at 40 °C the mancozeb decomposes.
- It would be better to give the exact pH value instead of pH 9.5 - 10
- One participant considered that the pH range relates to the column type, which should be resistant at high pH values
- One participant raised the problem of purity of the used standard and the applicability of the method for other dithiocarbamates. The answer was that the standard was purified in-house and the method can be used also for other dithiocarbamates.
- One participant asked why sodium sulphite is used, and why Solution A should not be used after 24 hours. The answer was that the solution decomposes in time. It was proposed to use the remark: freshly prepared solution should be used.
- What compound is detected during the HPLC measurement? There was no unequivocal answer.
- There were some comments on the selectivity of the method. It is not selective.
- What is the difference between the two lines on slide 18? One line was the existing CIPAC method the other is the proposed CIPAC method.

Closed Meeting:
It was proposed for full scale collaborative trial with some notes: the recommended temperature possibly be 30 °C, clarification of the pH value of the eluent and its usability with the column, the importance of using the proper analytical standard. It was proposed to change the wording to "freshly prepared" instead of "not after 24 h". The Company should also provide an identity test.

CIPAC STATUS REPORT

16/09/2020

CIPAC 61th meeting, June 2017 in Rome

Mr Li Liunhu presented the results of a full-scale trial for the determination of mancozeb in TC and WP formulations by HPLC. 18 laboratories sent back the results in time; the statistical evaluation was carried out based on their results.
Five samples were sent to the participants, two technical materials and three WP formulations.
Mancozeb was determined by reversed phase high performance liquid chromatography using UV detection at 282 nm and external standardization.
After the elimination of outliers and stragglers the between laboratory experimental relative reproducibility standard deviation (% RSDR) was below the calculated acceptable value based on the Horwitz's curve calculation for the mancozeb technical and WP samples.
Therefore, the organizer of this trial considered that the method is suitable for the intended purpose and recommended accepting it as a provisional CIPAC method for the determination of mancozeb in TC and WP formulations.

The following comments were received from the meeting:

- One participant asked if purified standard material was used and if yes, then how did the laboratory purify the standard? Technical standard was used and was not further purified.
- It was asked whether a commercially available standard was tested and compared with the technical material. The laboratory compared their standard with the commercially available reference material.
- One participant expressed some concerns regarding the stability of mancozeb and mentioned that in some cases it was difficult to solubilise the sample. Degradation during analysis was also observed.
- Big variation between the two days' measurements data was observed by several participants
- What was the purity of used standard? The purity of standard was 86%.
- Did the laboratory use own produced reference material and if this was compared with the commercially available? The laboratory used their own production standard and compared the used standard with the commercially available one.
- Did the laboratory use the presented HPLC method for characterising the standard material? The HPLC method was used.

Closed Meeting:
A full scale collaborative trial was presented, the following comments were received:

- -The proposed method had lots of problems, the standard couldn't be properly dissolved in the indicated solvent, the peak areas were not stable, the measurements carried out on consecutive days were not similar.
- Other participants on the trial agreed with the first comment and further observations were received:
- -FTIR technique is not an acceptable tool for quantitative analysis of the reference material?
- -For stability reasons and to reduce hydrolysis, the pH should be kept at higher values, instead of 9 at values of 9.5-9.9.
- -Due to the stability problems in many cases differences between the two days' measurement were observed
- -Mancozeb is a complicated mixture which is very sensitive to temperature and pH
- Some recommendations were received:
- -To increase the sonication time to 30 min.
- -To adjust the pH to 9.9 for stability reasons.

The opinion of the meeting was that additional data will be requested for this method.

CIPAC 62nd meeting, June 2018 in Panama City

Mancozeb by Mr Li Linhu (5146, 5147)
Mr Li Linhu presented the results of an additional CIPAC collaborative trial for mancozeb in two technical materials and three wettable powders. The additional trial was the result of method improvement suggestions made at the 61st CIPAC annual meeting (Rome, 2017). The original analytical method was modified with respect to environmental control (not controlled changed to 17±1°C), the length of the HPLC column (250 changed to 150 mm), HPLC column temperature (30 °C changed to 15 °C), pH of the mobile phase (9.5 changed to 10), composition of solution B (1 g/l sodium sulfite and 10 mM EDTA, pH 10.8 changed to 3 g/l sodium sulfite and 20 mM EDTA, pH 11.0), and the weight of the sample (100 mg changed to 40 mg).
Four laboratories participated in the trial, three from China and one from Europe. Three participants used the recommended conditions during the trial and reported no deviations or comments.
However, the fourth laboratory struggled with the method and had to repeat the experiments for six days.
The organizers decided to exclude the data of the fourth laboratory from the statistical data evaluation according to DIN ISO 5725. No Cochran's or Grubb's stragglers or outliers were identified and the Horwitz criteria were met for all three samples. HorRat values of 0.14, 0.11, 0.14, 0.26 and 0.24 were reported for TC-1, TC-2, WP-1, WP-2 and WP-3 respectively.
The organizers recommended that the method should be accepted as a provisional CIPAC method.

The following comments were received from the meeting:

- Mr Haustein remarked that the key issue is the temperature of the column and that of the laboratory and an environmental temperature of 17±1oC is very difficult to maintain for the average pesticide control laboratories.
- Mr Garvey remarked that at an environmental temperature of >20 oC the EDTA complex is breaking down, resulting in clogging of the HPLC system.
- Mr Ramesh proposed to cool the samples to lower temperatures before the analysis in a cooling chamber.
- Mrs Bos remarked that it is needed to use the same purity reference standard as the samples for solubility reasons, otherwise the results will be not correct.
- Mrs Bos asked whether the analysis would provide reliable answers when other WP concentrations than the tested concentration of 81% had to be determined. She expressed her concern of the correctness of the results if a 90% pure analytical standard is used to analyse a 50 % sample, for example. Mr Linhu answered that this was possible but again doubts remained about the validity of the answer.
- Mr Garvey remarked that the chromatographic peak resulted from an EDTA complex and not as such from mancozeb. Therefore, the retention time was not a reliable identification parameter. This was seconded by Mrs Bos and Mr Pigeon as they stated that other dithiocarbamates (e.g. maneb) would elute at exactly the same retention time. Mr Hänel remarked that FTIR could be used as identity test. Mr Garvey and Mr Haustein suggested to use LC-MS for identification. Mr Haustein also suggested to use the identification method which is prescribed when using the current titration based method for mancozeb. From the audience came also the remark that the identity might also be proven by using the UV absorbance spectrum. Mr Linhu answered that mancozeb is not amenable for LC-MS analysis, this is why they use IR.
- Mr Hänel concluded that many questions still existed and that the answers were not always sufficient to satisfy the audience. He proposed to try to analyse a sample of for example 50% purity with a standard of higher purity, also using the cooling chamber proposed and see if this works.

Closed Meeting:
Additional work is required and Mr Hänel and Mr Bura will contact Mr Linhu about the extent of the work. It was proposed to repeat the study with formulations of different compositions, for example those provided by Mrs Bos to the company using the proposal of sample preparation of Mr Ramesh. Especially the focus should be on:

- testing lower concentrations than the reference
- testing whether the environmental conditions of <17°C are required
- testing the analysis with maneb and to resolve the identification issue (can the method differentiate between maneb and mancozeb).

CIPAC 63rd meeting, June 2019 in Braunschweig

Mancozeb by Ms Junhua Song (5157, 5158)
Mrs Junhua Song presented the results of a large scale CIPAC collaborative trial for mancozeb in two TCs and three WP formulations. The large scale trial included method improvements resulting from the 62nd CIPAC annual meeting (Panama, 2018) about the temperature of the analytical column (<20°C), stability of the EBCD-anion (stable for 4 hrs at 20±2°C), and the identity test by adding MT 154 (differentiation of Zn-containing dithiocarbamates) and MT 165 (differentiation of Mancozeb with Maneb and zinc).
Furthermore the results of the proposed method were compared with CIPAC method 34 with good results: 50.4%, 50.8%, and 50.8% by the CIPAC method and 50.4%, 50.6%, 50.8% by the proposed HPLC based method.
Eight laboratories participated in the trial, six from China, one from Europe, and one from Central-America. Unfortunately, Lab 1 encountered custom problems resulting in a very late arrival of the samples (>1 month after shipment).
All participants used the recommended conditions during the trial with the exception of lab 3 which used a longer HPLC column (250 mm instead of 150 mm) and adjusted the flow rate accordingly (1.3 ml/min instead of 1.0 ml/min). The 4 hrs stability period was ignored by all participants as the sequence containing all samples was considerably longer than 7 hrs.
Remarks were received from the participating laboratories about the non-specificity of the HPLC method, about the use of non-certified reference material, changes in the injection sequence, and the use of 0.45 µm filters instead of 0.22 µm filters.
The data of all participants were included in the statistical evaluation (according to DIN ISO 5725) while applying the Cochrans' and Grubbs tests for stragglers or outliers. The results of lab 1 were identified as Cochran outliers for TC-1, TC-2, WP-1, and WP-2. Furthermore they were also identified as Grubbs stragglers for TC-1, WP-1, and WP-3.
Horwitz criteria were met for all five samples whether or not the outliers and stragglers were included. Unfortunately, no HorRat values were reported.

The organizers recommended that the method should be accepted as a provisional CIPAC method.

The following comments were received from the meeting:

- Mr Manso remarked that the method will not work in combination with other actives. Ms Xu Mei replied that the method was developed for formulations that contain only mancozeb.
- Mr Haustein remarked that the HorRat value should be included in the report. Mr Hänel replied that due to an unforeseen communication error the document about the application of the Horrat value was not available from the website but that this omission soon would be rectified.
- Mrs Vinke remarked that only samples with high amounts of mancozeb were investigated and was curious whether formulations with lower amounts of mancozeb were investigated. This was not the case.

Closed Meeting:
A large scale trial was presented and the method can be promoted to a **provisional CIPAC method**. Some discussion arose whether the large number of Chinese participants (75%) could be regarded as a regional collaborative trial. In the end this was judged not to be the case. In addition, the HorRat-value for the trial should be calculated and in case that the results need a justification, this should be provided to the CIPAC secretary.

CIPAC STATUS REPORT

16/09/2020

CIPAC 64th meeting, June 2020 virtual (Geneva, Corona)

The reversed phase HPLC method (CIPAC/5209) for the determination of hexaconazole in TC, WG and SC formulations was accepted as a **full** CIPAC method. The HorRat values should be calculated and reported.

CIPAC 64th meeting, June 2020 virtual (Geneva, Corona)

The reversed phase HPLC method (CIPAC/5157) for the determination of mancozeb in TC and WP formulations was accepted as a **full** CIPAC method with some precisions in the description of the method.