Van: **Vinke, Dr. Claudia** claudia.vinke@bvl.bund.de
Onderwerp: Problems regarding the CIPAC method Mancozeb 34/TC/M/- and 34/WP/M/-
Datum: 28 mei 2020 om 15:06
Aan: BURA Laszlo Laszlo.BURA@efsa.europa.eu

CV

Dear Laszlo,

I hope you and your family are fine and healthy.
I have some remarks regarding the new CIPAC method for Mancozeb.

As the new CIPAC method for Mancozeb could save time compared to the titration method we performed some studies with HPLC. Unfortunately, in Germany there is no WP product available so we used standard material from Dr. Ehrenstorfer, which is stable until March 2022.
We were faced some problems:
It was not possible to solve the standard according to the method description using ultrasonic only. After 65 min still some solid particles were visible. A complete dissolution was possible by manually shaking the standard solution for 2.5 min. Using a horizontal shaker with about 100 rpm dissolution was completed after 13 min.
According to the method you need a minimum of 60 min to check the stability of standard solution C1 and additional a minimum of 30 min to check the quality of C2 compared to C1. We checked the stability by injecting C1 20 times in a row. The first 2 injections were outliers according to Dean&Dixon and had to be discarded. Therefore, we needed 90 min for checking the C1 stability. With an overall stability of 4 h for the standard solutions and sample solutions there are maximum 3 h left, realistically only 2.5 h for analysing samples. In a row, you can only analyse maximum 4 samples. Regarding our intra-lab requirements on method validation we are not able to validate the method in one sequence with repeatability, linearity and recovery.
The method gives no information regarding the differences in the peak areas of C2. In one measurement we found a difference of 1.19 % between injection 1 and injection 2. Is this acceptable?
For the measurement we used an Eclipse Plus C18 column (4.6 x 50 mm, 1.8 µm) instead of an Agilent Extent C18 (4.6 X 150 mm, 5 µm). This results in a retention time of approximately 3.1 min instead of approximately 7.5 min. In the method it is mentioned that also an equivalent column can be used. From the column material the column we used is equivalent. But we were faced a shift in the retention time during the measurement. In the stability test for C1 we observed a shift in the retention time. Taking the Dean&Dixon outlier into account the shift compared to the 1. Injection was higher than the given 0.5 % after 12 injections. Discarding these outliers, the shift was higher than 0.5 % after 13 injections. We also measured a sample from 2018 (WG formulation) and in this sequence we found a shift in the retention time for C1, too. This shift was higher than 0.5 % after 5 injections. But the method allows a shift of 1.5 %, so everything is okay.
Regarding the sample from 2018 (a WG formulation) the HPLC method gave a concentration of Mancozeb of 595 g/kg, which is out of specification as the content should be 680 g/kg. The titration method performed in February 2019 gave a concentration of 692 g/kg. A repetition of the titration method is still pending but it seems unlikely that the degradation of Mancozeb in a formulation is 14 % in 15 months. We can report the results of the titration after we repeated the study.
It is a pity that there are no WP formulation on the German market, otherwise we would do some further studies. If there is a possibility to get a WP formulation I would be happy to get a sample to perform some further studies with the method.

I have one additional remark regarding the values for the repeatability r and the reproducibility R given in the method. The values are given in g/kg and not in %. Calculating the relative values for the TC with 850 g/kg r is between 1.06 % and 2.24 % and R is between 1.76 % and 2.82 %. Calculation of the Horwitz value for this concentration gives a Horwitz-RSDr of 1.37 % and a Horwitz-RSDR of 2.05 %. That means that r and R is partly higher than given by Horwitz. For the WP formulation with 830 g/kg the situation is even worse. I wonder whether this is acceptable for a CIPAC method as according to the "CIPAC Guidelines for Collaborative Study Procedures for Assessment of Performance of Analytical Methods" the reproducibility R should not be larger than the Horwitz-RSDR.

As Ralf is the chair of CIPAC I did not ask him for his opinion regarding our results. But he knows that I inform you.
For any questions please do not hesitate to contact me. But please be aware that I will be out of office in July and August.

Best regards
Claudia

Dr. Claudia Vinke
Bundesamt für Verbraucherschutz und Lebensmittelsicherheit
Abteilung Pflanzenschutzmittel

Messeweg 11/12
38104 Braunschweig
Tel.: 0531 299 3540
Fax: 0531 299 3002
E-Mail: claudia.vinke@bvl.bund.de
Internet: https://eur03.safelinks.protection.outlook.com/?
url=http%3A%2F%2Fwww.bvl.bund.de%2F&data=02%7C01%7C%7C68404efd6de947d6365708d803
07eeec%7C406a174be31548bdaa0acdaddc44250b%7C1%7C0%7C637262679899226286&sdata=b
80sbrPdoyKk0M8reAgiG81mp36el0EpFey%2F0MbeLXI%3D&reserved=0

PRIVACY POLICY INFORMATION: https://eur03.safelinks.protection.outlook.com/?
url=https%3A%2F%2Fwww.bvl.bund.de%2Fprivacy-
policy&data=02%7C01%7C%7C68404efd6de947d6365708d80307eeec%7C406a174be31548bdaa0a
cdaddc44250b%7C1%7C0%7C637262679899226286&sdata=kzJGd%2FvdpRv%2BTx53iJXIYP8laEq
19uJj4cDanVwLBKg%3D&reserved=0