Determination of ethylenebis dithiocarbamates in formulated products by HPLC

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Objectives

Ethylenebis dithiocarbamates (EBDCs) are broad spectrum fungicides introduced in the early 1940s. They are widely used to protect many fruit, vegetable and field crops against key diseases including blights, mildews and scabs on potatoes and tomatoes.

Maneb, zineb and mancozeb are EBDC polymeric complexes with manganese or / and zinc metal ions. Their poor solubility in water and in organic solvents leads to difficulty to determine their content in formulated products.

CIPAC methods recommended in FAO specifications consist in decomposition with acid and titration of the liberated carbon disulfide. They need huge preparation and are not specific. An improvement would be the development and validation of a chromatographic method by HPLC-DAD.

Late blight on potato leaf
Photo: Howard F. Schwartz, Colorado State University, Bugwood.org

Method

Reagents (aqueous solutions)

EDTA tetrasodium salt 5% w/v solution
(to solubilise EBDC by chelation of metal ions)
Ammonium formate 10 mM solution, pH10

Calibration solution

120 mg EBDC in 200 mL
+ 5 mL water and 10 mL EDTA
+ ammonium formate solution
Dilution 2.5 mL/100 mL
in ammonium formate solution

Preparation of sample

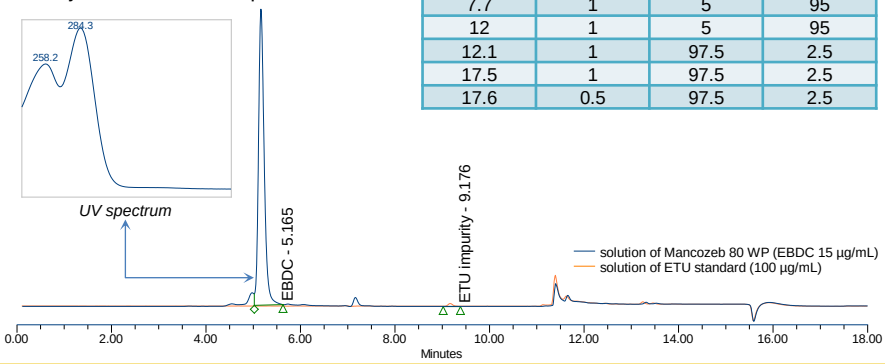
- 80% w/w WP and 75% w/w WG:
  750 mg EBDC in 500 mL water
- 500 g/L SC:
  300 mg EBDC in 200 mL water

Dilutions in ammonium formate solution:
1) 5 mL/50 mL (+ 10 mL EDTA)
2) 5 mL/50 mL

Operating conditions

HPLC column: Phenomenex Gemini® C6-Phenyl, 5 µm, 250 x 4.6 mm i.d.
Mobile phase: gradient elution
Column temperature: 25°C
Detector wavelength: 285 nm
Injection volume: 10 µL

Time [minutes]	Flow rate [mL/min]	Ammonium formate solution [%]	Methanol [%]
0	0.5	97.5	2.5
1	0.5	97.5	2.5
7.5	0.5	95	5
7.6	1	95	5
7.7	1	5	95
12	1	5	95
12.1	1	97.5	2.5
17.5	1	97.5	2.5
17.6	0.5	97.5	2.5



Partial validation results

	Mancozeb	Maneb	Zineb
Linearity checked on 5 points between 5 - 25 µg/mL	r = 0.9999	r = 0.9999	r = 1.0000
Repeatability (n = 6) of:	Relative standard deviation (RSD)		
➢ Injections	0.17%	0.34%	0.21%
➢ Extraction (separate dilutions from a stock solution)	0.59%		
Repeatability (n = 6) (separate weighings):	Results obtained (% w/w, criteria: $RSD_r < RSD_r(Hor)$ (Horwitz value x 0.67))		
80% w/w WP	79.28 RSD_r: 1.25% < $RSD_r(Hor)$: 1.39% (*CIPAC method*: *79.73*)	81.18 RSD_r: 1.26% < $RSD_r(Hor)$: 1.38%	
75% w/w WG	76.04 RSD_r: 0.92% < $RSD_r(Hor)$: 1.40% (*CIPAC method*: *76.44*)	75.98 RSD_r: 2.25% > $RSD_r(Hor)$: 1.40%	
500 g/L (37% w/w) SC	36.43 RSD_r: 0.55% < $RSD_r(Hor)$: 1.56%		
Stability of solutions	> 10 hours and < 23 hours		

The resolution of EBDCs peak should be improved by the use of:
➢ other column chemistry;
➢ UHPLC system.
It should give better repeatability.

The method has been easily adapted to determine EBDCs content in the remaining tenth after the test of suspensibility.

Conclusion

These results open perspectives for full development and validation of a new method to determine ethylenebis dithiocarbamates.

Reference: Klautzsch F., Lipinski J., Martens-Menzel R. (2008). *Stability of dithiocarbamates during the preparation and extraction of food samples*. 7th European Pesticide Residue Workshop, Estrel Convention Centre Berlin.

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