T. Pl.ziekten 65 (1959): 27–32.

THE DETERMINATION OF RESIDUES OF ZINC ETHYLENE BISDITHIOCARBAMATE[1]

Met een samenvatting:
De bepaling van residu's van zinkethyleenbisdithiocarbamaat

BY

M. C. KERSSEN and P. RIEPMA
Instituut voor Plantenziektenkundig Onderzoek, Wageningen

INTRODUCTION

It may be assumed that the effective control of plant diseases is related to the amount of chemical retained by the plant, and the distribution and persistence of the chemical.

Due to losses during spraying, to the properties of the leaves of the plants (bouncing off or running off of the droplets) and to weather conditions the amount retained will be mostly less than the amount applied. The distribution of the chemical depends on the volume applied and the droplet size. The persistence largely depends on the weather conditions after the application.

To establish the residual amount of active substance on the plants analytical methods have to be used. If a general view of the residue and the distribution of the spray in field crops is desired, many samples have to be taken, because of irregularities in growth, spraying etc. This requires the availability of rapid and simple analytical methods.

As long as inorganic compounds are used it is easy to find simple methods because organic reagents are available for a spectrophotometric determination of metals (SNELL & SNELL, 1949; MORRISON & FREISER, 1957). The detection of organic compounds is more difficult unless these are already used for the determination of traces of metals. In the latter case modifications of the original method have to be introduced. This has to be done to achieve a simple method to determine residues of dithiocarbamates.

CLARKE et al. (1951) determined residual amounts of dithiocarbamates by leading CS_2, a breakdown product of these pesticides, into a solution of triethanolamine, diethylamine and copperacetate in alcohol to form the copper salt of diethyldithiocarbamic acid. The colour intensity of this salt, measured spectrophotometrically, may be related to the amount of residue of the dithiocarbamate. However, this method requires an apparatus, which limits the number of samples that can be determined. Therefore it seemed more appropriate to change the original method of MCFARLANE (1932), using diethyldithiocarbamate as a reagent to determine traces of copper. When an aqueous solution of sodium diethyldithiocarbamate is added to a solution containing copper the copper salt of diethyldithiocarbamic acid, which has a golden brown colour, is formed.

---

[1] Accepted for publication 1 December, 1958.

METHOD OF ANALYSIS

Reagents:

Copper sulfate: 1875 mg $CuSO_4.5H_2O$ diluted to 4000 ml.
Sodium hydroxide: 20 g NaOH diluted to 1000 ml.
Sodium pyrophosphate: 30 g $Na_4P_2O_7.10H_2O$ diluted to 1000 ml.

These reagents were added in various volumes to the test solution to investigate the most suitable conditions for the determination of dithiocarbamates, especially of zinc ethylene bisdithiocarbamate.

EXPERIMENTAL RESULTS

From preliminary experiments it was evident that the maximum optical density of the copper salt of ethylene bisdithiocarbamic acid occurred at a wave length of 4340 Å, the same as that for the copper salt of diethyldithiocarbamic acid.

It was observed that the alcalinity of the solution greatly influences its optical density (fig. 1). Excess of the amount of NaOH in the test solution reduces the optical density of the copper salt of ethylene bisdithiocarbamic acid significantly. Beer's law was valid only when the amount of copper reagent in the test solution did not exceed a certain threshold. The cause is the low solubility of the copper salt of the dithiocarbamic acid. The upper limit of the amount of copper, investigated with the aid of sodium diethyldithiocarbamate, was shown to be 250 μg in 10 ml solution.

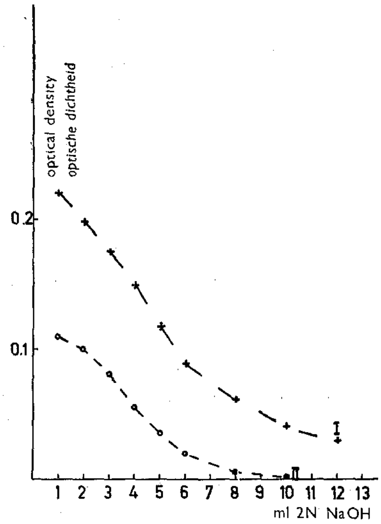

FIG. 1. The relation between the alcalinity of the solution, expressed in ml 2 n NaOH and the optical density of the copper salt of ethylene bisdithiocarbamic acid. The volume of the test solution was 50 ml. This solution contained next to increasing volumes 2 n NaOH, 30 mg sodium pyrophosphate and:
I. 1000 μg Cu and 2000 μg zineb (commercial product);
II. 1000 μg Cu and 1000 μg zineb.

Het verband tussen de alkaliteit van de oplossing, uitgedrukt in ml 2 n NaOH en de optische dichtheid van het koperzout van ethyleenbisdithiocarbaminezuur. Het volume van de oplossing was 50 ml. Deze oplossing bevatte behalve toenemende volumina 2n NaOH, 30 mg natriumpyrofosfaat en
I. 1000 μg Cu en 2000 μg zineb (handelsprodukt)
II. 1000 μg Cu en 1000 μg zineb.

The suspension may be stabilized by adding a drop of Teepol to the solution.

Next to the active substance commercial products contain contaminations, which may interfere with the spectrophotometric determination of the dithiocarbamates. According to McFarlane (1932) especially ions of iron and zinc may reduce the optical density of the copper salts of the dithiocarbamic acids.

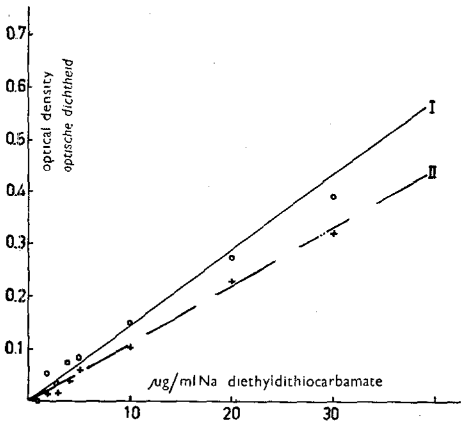

FIG. 2.

The effect of sodium pyrophosphate on the optical density of the copper salt of diethyldithiocarbamic acid in the presence of ferric ions.

I. Test solution with $Na_4P_7O_2.10H_2O$;
II. Test solution without $Na_4P_7O_2.10H_2O$.

De invloed van natriumpyrofosfaat op de optische dichtheid van het koperzout van diethyldithiocarbaminezuur in aanwezigheid van ferri-ionen.

I. oplossing met $Na_4P_2O_7.10H_2O$;
II. oplossing zonder $Na_4P_2O_7.10H_2O$.

Addition of sodium pyrophosphate abolishes the interference of these ions (fig. 2). The action of sodium pyrophosphate has to be ascribed to the precipitation of the insoluble $Fe_4(P_2O_7)_3$, whereas the reactivity of $Cu_2P_2O_7$ is not affected. Presence of 345 µg Fe (salt $FeCl_3$) in 20 ml test solution diminishes the optical density of the copper salt of diethyldithiocarbamic acid if the sodium pyrophosphate is left out of the test solution. The regressions between the optical density and the concentration of sodium diethyldithiocarbamate in the presence and absence of sodium pyrophosphate were 0.0126 and 0.0111, respectively.

The most suitable composition of the test solution was found to be 30 mg $Na_4P_2O_7.10H_2O$, 2 ml 0.5 n NaOH and 375 µg Cu in a volume of 16 ml. Deviations of BEER's law may occur if the concentration of zineb exceeds 500 µg in this volume (fig. 3).

Once established the right composition of the test solution experiments con-

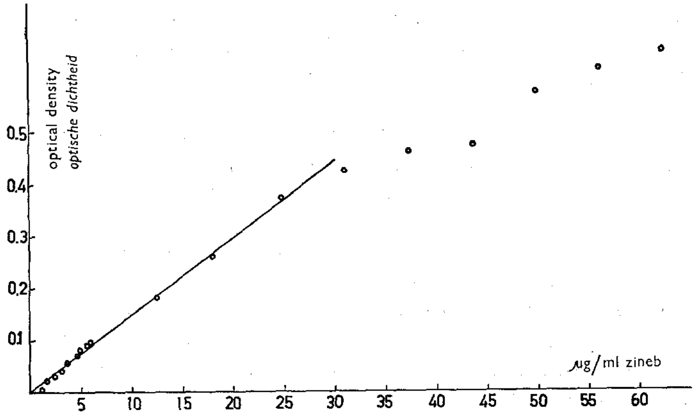

FIG. 3. The relation between the concentration of zineb and the optical density of its copper salt, after the establishment of the right composition of the test solution.

De samenhang tussen de concentratie van zineb en de optische dichtheid van het koperzout nadat de juiste samenstelling der oplossing was vastgesteld.

cerning the possibility to recover known amounts of residue from glass plates and leaves of plants were carried out. The results of one experiment are presented in table 1.

TABLE 1. The amount of zineb recovered from different surfaces in the course of time.
De hoeveelheid zineb, die na verloop van tijd op verschillende oppervlakken werd teruggevonden.

Surface *Oppervlak*	Amount of zineb applied in µg *Toegediende hoeveelheid zineb in µg*	Zineb recovered in µg *Teruggevonden zineb in µg* days after application *dagen na toediening*			
		0	6	13	20
Glass plates (about 20°C)	1628	1656 ± 78	1406 ± 13	1352 ± 104	1501 ± 130
Brassica	3256	3388 ± 88	2847 ± 380	1122 ± 272	1006 ± 260
Phaseolus	3256	3586 ± 210	2822 ± 110	1361 ± 176	1227 ± 185

The zineb residues, applied to the glass plates with a pipette, were left till dried and afterwards stored in the dark. After 0, 6, 13 and 20 days the residual amounts of zineb were determined. The results are presented in table 1. It is evident that the residues brought onto the glass plates may be recovered quantitatively, because no significant differences between applied and recovered amounts of zineb could be found if the residue was determined immediately after the application (0 days). The same holds true if a suspension of zineb is applied to the leaves of Brassica and Phaseolus with a pipette. Differences between applied and recovered amounts of residue have to be ascribed to the manner of application.

From the data it is evident that the residue of zineb on the glass plates, held in the dark at 20 °C, is not affected during 20 days. The keeping of residues of zineb on glass plates at other temperatures (0 ° and 30 °C) in the dark or at 20 °C in diffuse daylight during the same time did not affect the breakdown of this product.

However, if the residues of zineb, applied to the leaves of plants, are determined after different times of exposure to greenhouse conditions (mean temperature: 20 °C; solar radiation) it is observed that a steady decrease of the residue occurs.

Determination of the amount of residue of zineb was made by washing the glass plates and the leaves with two portions of 40 ml aq. dest. after adding three drops of Teepol. To recover the zineb quantitatively off the glass plates it was necessary to wipe these with a rubber. Omitting the wiping resulted in the sticking of a part of the residue to the glass plates (table 2). Also the leaves have to be cleaned thoroughly.

A radiation energy on three successive days of 505, 543 and 603 cal/cm^2 could not reduce the original amount of zineb residue sprayed on potato foliage. The values expressed in those of the original amount were found to be 100.2 %, 118 % and 89 %.

TABLE 2. The effect of the wiping off of glass plates on the recovery of zineb residues applied. *De invloed van het afvegen van glasplaten op het terugvinden van residu's van daarop aangebrachte zineb.*

Number of days after application *Aantal dagen na toepassing*	Amount of zineb applied in µg *Hoeveelheid toegediende zineb in µg*	Recovery of zineb in µg *Teruggevonden hoeveelheid zineb in µg*	
		80 ml water used for washing *afgespoeld met* 80 *ml water*	after washing wiped off with 40 ml water *na spoelen afgeveegd met* 40 *ml water*
0	1628	1694 ± 78	82.5 ± 6.5
2	1628	1612 ± 41	490 ± 30
7	1628	1227 ± 42	157.6 ± 9.7

On a later date 12.0 mm rain reduced the original amount of zineb deposit with 68 % over the same period. These findings indicate that rainfall is the major agent reducing the residue of zineb. Even 4.5 mm of rainfall may reduce the original deposit of zineb with 67 %. It may be assumed that the reduction of zineb residue not only depends on the amount of rainfall, but also on its intensity.

DISCUSSION AND SUMMARY

The method described is meant to determine the amount of residue of zineb upon the surface of leaves and glass plates. The total amount of residue of this product cannot be determined this way if penetration into the leaves occurs. In that case the methods described by CLARKE et al. (1951) may prove more suitable, because it recovers the breakdown products of zineb and other dithiocarbamates during the ashing of the leaf tissues. But even then large errors may be observed as is evident from the data presented by the authors, concerning the recovery of disodium ethylene bisdithiocarbamate. Using the micromethod they could only recover 79 % of the amount supplied. If disodium ethylene bisdithiocarbamate was applied to potato foliage the authors recovered about 80 %. By comparing their data and ours, as presented in table 1, we found our method to be suitable for the recovery of zineb residue on surfaces.

The stability of zineb under laboratory conditions is in accordance with their observation. However, if zineb is applied to potatoes in the field, the product disappears rapidly, due to the weather conditions (rainfall, dew and solar radiation). From field observations it may be concluded that solar radiation plays a minor role in the loss of activity of zineb in contrast to rainfall.

SAMENVATTING

Een methode wordt beschreven volgens welke op eenvoudige wijze zinkethyleenbisdithiocarbamaat (zineb) kan worden bepaald op glasplaten en bladeren. Deze methode is geschikt om de hoeveelheid zineb te bepalen, die op bladeren en glasplaten terecht komt bij een bespuiting, alsmede ter vaststelling van de persistentie van het produkt onder invloed van uitwendige omstandigheden, voorzover het produkt niet in de bladeren binnendringt. De meest geschikte oplossing, waarin zineb kan worden aangetoond, bleek de volgende hoeveelheden stoffen te moeten bevatten op een totaal volume van 16 ml: 30 mg $Na_4P_2O_2.10H_2O$, 2 ml 0,5 n NaOH en 375 μg Cu. De wet van BEER geldt, zolang de hoeveelheid zineb in deze oplossing niet stijgt boven 500 μg. Toevoeging van Teepol is noodzakelijk om de suspensie van het koperzout van ethyleenbisdithiocarbaminezuur te stabiliseren. Toevoeging van natriumpyrofosfaat aan de oplossing dient om te voorkomen dat de gevoeligheid van de beschreven methode onder invloed van ijzer- en zinkionen vermindert.

Uit proeven, waarbij bekende hoeveelheden zineb op glasplaten en bladeren werden aangebracht, blijkt dat de toegediende hoeveelheden kwantitatief kunnen worden teruggevonden. De behandelde oppervlakken dienen zorgvuldig te worden afgewassen. Blootstelling van het residu aan verschillende temperaturen of aan diffuus daglicht heeft geen achteruitgang van de hoeveelheid actieve stof op korte termijn (20 dagen) tengevolge.

REFERENCES

SNELL, F. D. & C. T. SNELL, – 1949. Colorimetric methods of analysis.

MORRISON, G. H. & H. FREISER, – 1957. Solvent extraction in analytical chemistry.

MCFARLANE, W. D., – 1932. Application of the sodium diethyldithiocarbamate reaction to the microcolorimetric determination of copper in organic substances. Biochem. J. 26: 1022–1033.

CLARKE, D. G., H. BAUM, E. L. STANLEY & W. F. HESTER, – 1951. Determination of dithiocarbamates. Anal. Chem. 23: 1842–1846.