Аграрен университет – Пловдив, Научни трудове, т. LIV, 2009 г.
Девета научнопрактическа конференция "Екология, земеделие, животновъдство", Агроеко 2009
Agricultural University – Plovdiv, Scientific Works, vol. LIV, 2009
Ninth Scientific Practical Conference "Ecology, Agriculture, Animal Husbandry", Agroeco 2009

# DETERMINATION OF MANGANESE IN PLANT SAMPLES

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## INTRODUCTION

Manganese is one of the microelements which are actively absorbed by plants. The biological absorption coefficient for manganese is greater than those for the other microelements in this group /Zn, Cu, Mo, Ni, Co, Pb/. The formation of the plant mass depends on the manganese provision for the plants. Manganese takes part in a number of important physiological and biological processes in the lower and higher plant organisms - in the nitrogen metabolism, photosynthesis, breathing and maintaining the needed oxidation-reduction conditions in the cell.

The optimal content of manganese, its critical level and toxic concentration at which the growth is depressed and the yield decreased, have been established for a great number of crops [4].

Various methods for determination of manganese have been published. Analyses with some reagents are used [1, 2, 3, 5, 7, 8].

The present study is intended to clear up the effect of a prolonged fertilization (mineral and organic) on the manganese content in radishes using a new extraction-photometric method with Crystal Violet for determination of manganese. To show that the triphenylmethane dye Crystal Violet which we used for the first time, can be applied to the analysis of manganese in plant material.

## MATERIAL AND METHODS

An analysis for manganese content by variants of averaged root samples was carried out using a new extraction-spectrophotometric method with Crystal Violet. Manganese(VII) forms an ion-association complex with triphenylmethane dye Crystal Violet (CV). To clear out the possibility of extracting the ion associate a number of different types of organic solvents were tested: hydrocarbons (benzene and toluene), ethers, ketones, alcohols, chloroform, dichlorethane and tetrachlorethane. The studies showed that the associate is best dissolved in 1,2-dichloroethane. Maximum light absorption of the associate is observed at 250 nm.

## Apparatus

Spectrophotometer VSU with 1-cm light path quartz cells.

### Procedure

A wet burning of the plant sample was carried out in which a mixture of sulphuric and nitric acids was used for the oxidation of the organic substance. A portion of 2 g of air-dry plant material was placed into a Kjeldal flask and moistened with 4 ml distilled water. 5 ml conc. sulphuric acid and 10 ml conc. nitric acid were added. The flask was slightly heated to avoid splashing of the solution decomposition and fuming away of $HNO_3$. If the oxidation of the organic substance was not completed, $HNO_3$ was added and heated again. When all the organic material was oxidized, the solution was heated at a higher temperature for 10 min. After cooling the solution was diluted with water and filtered. It was heated to boiling point and the temperature was maintained for 10 min [6]. After cooling the solution was diluted with water and filtered. It was transferred into a volumetric flask of 50 ml and diluted to the mark with distilled water. Aliquot parts of this solution were taken for analysis.

In separatory funnel of 100 ml are introduced the solutions: 0.3 ml hydrochloric acid 1.2 M, 0.4 ml Crystal Violet $1x10^{-3}$ M, aliquote of the prepared solution of plant sample. It is diluted up to a volume of the aqueous phase of 10 ml with distilled water and extracted with 3 ml of 1,2-dichloroethane for 30 s. The organic phase is filtered through a dry paper into a 1 cm cuvette and the absorbance measured at 250 nm. A blank is run in parallel in the absence of plant sample. A calibration graph is constructed with standards similarly treated.

### RESULTS AND DISCUSSION

The mineral fertilization brought to considerable changes of the manganese content in the radishes (Table 1). Manganese is determined with a new extraction-photometric method.

As we take into account the different fertilization with N, P and K (Variants 2,3,4) it can be seen that radish accumulate least manganese 10 mg /kg in fertilization only with P and K ($N_0P_{120}K_{120}$) (Variant 4). The content of manganese grows up above 5 times if in the fertilization can be used a nitric fertilizer $N_{120}P_{120}K_0$ (Variant 2) and $N_{120}P_0K_{120}$ (Variant 3).

In a constant level of potassium $K_{120}$, manganese content increased with the increase of the fertilization norm of phosphorus. It is well expressed in the three levels of nitrogen fertilization with $N_{120}$, $N_{240}$ and $N_{360}$.

Table 1. — Manganese content in radishes (mg/kg dry mass).

| N | Variants | NPK Method with CV Mn mg/kg | Reliab. P= 99 % | RSD* % | Yield kg/ha |
|---|---|---|---|---|---|
| 1 | $N_0P_0K_0$ | 20.00 | a | 1.2 | 6325 |
| 2 | $N_{120}P_{120}K_0$ | 52.25 | d | 0.9 | 7480 |
| 3 | $N_{120}P_0K_{120}$ | 56.00 | b | 1.5 | 6325 |
| 4 | $N_0P_{120}K_{120}$ | 10.00 | b | 1.6 | 7095 |
| 5 | $N_{120}P_{120}K_{120}$ | 15.00 | a | 1.1 | 10314 |
| 6 | $N_{120}P_{240}K_{120}$ | 21.75 | d | 1.4 | 10149 |
| 7 | $N_{120}P_{360}K_{120}$ | 48.50 | c | 1.2 | 12404 |
| 8 | $N_{240}P_{120}K_{120}$ | 59.75 | c | 1.5 | 10039 |
| 9 | $N_{240}P_{240}K_{120}$ | 63.25 | f | 1.4 | 8279 |
| 10 | $N_{240}P_{360}K_{120}$ | 95.25 | a | 0.9 | 6875 |
| 11 | $N_{360}P_{120}K_{120}$ | 20.25 | e | 1.3 | 11964 |
| 12 | $N_{360}P_{240}K_{120}$ | 26.00 | d | 1.5 | 9790 |
| 13 | $N_{360}P_{360}K_{120}$ | 32.25 | b | 1.1 | 9295 |
| 14 | $N_{240}P_{240}K_{240}$ | 30.25 | f | 1.4 | 15261 |
| 15 | $N_{360}P_{360}K_{360}$ | 66.25 | c | 1.2 | 11935 |
| 16 | $N_{480}P_{480}K_{360}$ | 71.75 | a | 1.5 | 1359 |

*Relative Standard Deviation for CV method (n = 6)
a, b, c, ....A degree of reliability

Variants 5,6,7 with fertilization norm $N_{120}$ comprise 15 mg/kg, 21.75 mg/kg and 48.50 mg/kg Mn dry mass. Manganese has a strong positive influence on yield of radishes.

In a fertilization norm $N_{240}$ (variants 8,9,10) the content of manganese grows up 59.75 mg/kg, 63.25 mg/kg and 95.25 mg/kg with the increasing of the content of phosphorus. With the increasing of the concentration of manganese, the yield strong decreases.

The above-mentioned subordination can be seen in Variants 11,12,13 with $N_{360}$ , in which ones the content of manganese grows up too in 20.25 mg/kg, 26 mg/kg and 32.25 mg/kg. The subordination of yield from the content of manganese is negative.

A small negative correlation (R = - 0.18) determines the relation between the yield and the content of manganese in radishes in the variants from 1 to 16 (Fig. 1).

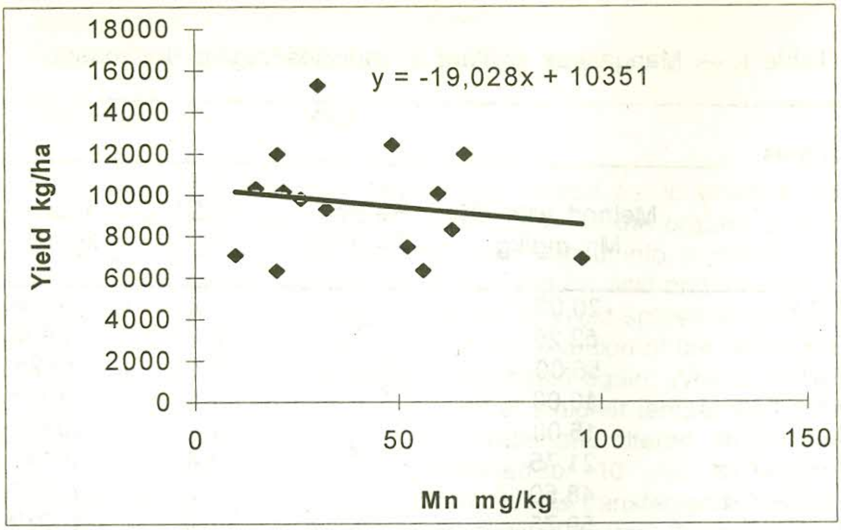


Fig. 1 A general subordination between yield kg/ha and the content of Mn in radishes with mineral fertilization; Correlation coefficient. R = -0.18

In the three levels of nitrogen fertilization with $N_{120}$, $N_{240}$ and $N_{360}$, the highest content here was 95.25 mg/kg Mn dry mass after fertilization with $N_{240}:P_{360}:K_{120}$ = 2:3:1.

Manganese content in radishes grows up with the increasing of the fertilization norm of N, P and K. Thus for instance in a fertilization with $N_{120}P_{120}K_{120}$ the content of manganese in radishes is 15.00 mg/kg (Variant 5). With the increasing of the fertilization norm of $N_{240}P_{240}K_{240}$, manganese also grows up to 30.25 mg/kg (Variant 14) ; in a fertilization norm $N_{360}P_{360}K_{360}$, the content of manganese is highes 66.25 mg/kg (Variant 15).

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