

# EFFICIENCY OF CHELATE FORMS OF MICRONUTRIENTS IN NUTRITION OF GREENHOUSE TOMATO GROWN IN ROCKWOOL

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## Abstract

Cultivation of vegetable crops on rockwool medium under controlled conditions requires the use of completely soluble forms of fertilizers for preparing nutrient solution. In order to prevent immobilization of metal microelements, especially Fe, they are often used in chelated forms. The low biodegradability of currently popular chelating agents may lead to contamination of the environment by these compounds. The aim of the present study was to evaluate whether it is necessary to use chelated forms of Cu and Mn. Another objective was to assess the applicability of two chelating agents of iron in cultivation of tomato on rockwool slabs. Mineral forms of manganese ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) and copper ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) were compared with EDTA+DTPA chelate forms of these nutrients. In the case of Fe, the suitability of EDTA and DTPA as the chelating agents was evaluated, taking into account the crop yield as well as nutritional status of tomatoes in different stages of growth. The results of our greenhouse trials proved that application of chelate forms of Cu and Mn did not alter the total yield of tomato fruits but accelerated fruit maturation, so that early tomato yield was higher than in response to mineral forms of these nutrients. Plants supplied with Cu and Mn chelates contained higher amounts of these nutrients in index parts of tomatoes analysed from May to August in one-month intervals. The use of DTPA and EDTA as chelating agents was just as productive in terms of tomato fruit yield. However, the DTPA chelate contributed to better plant nutrition with Fe, as well as Cu and Mn.

Key words: iron, copper, manganese, chelates, mineral forms, yield, nutrient status.

## SKUTECZNOŚĆ CHELATOWYCH FORM MIKROELEMENTÓW W NAWOŻENIU POMIDORA SZKLARNIOWEGO UPRAWIANEGO W WELNIE MINERALNEJ

### Abstrakt

Uprawa warzyw pod osłonami w welnie mineralnej wymaga stosowania pożywek, do których przygotowania stosuje się nawozy całkowicie rozpuszczalne w wodzie. Aby zapobiec uwstecznianiu mikroelementów metalicznych, przede wszystkim żelaza, często stosuje się formy chelatowe tych składników. Niektóre związki chelatowe, zwłaszcza EDTA, z powodu swojej trwałości mogą prowadzić do skażenia środowiska naturalnego. Przedmiotem badań była ocena zasadności stosowania chelatowych form miedzi i manganu oraz porównanie dwóch chelatów stosowanych do kompleksowania żelaza w uprawie pomidora szklarniowego w welnie mineralnej. Formy mineralne manganu ( $MnSO_4 \cdot H_2O$ ) i miedzi ( $CuSO_4 \cdot 5H_2O$ ) porównywano z chelatami EDTA+DTPA tych mikroelementów. W przypadku żelaza porównywano przydatność dwóch chelatów, tj. EDTA i DTPA, do nawożenia pomidora. W obydwu doświadczeniach oceniano wielkość plonu i stan odżywienia roślin mikroelementami w różnych stadiach rozwoju. Wykazano, że chelatowe formy Mn i Cu nie wpływały istotnie na plon ogółem owoców pomidora, przyczyniły się jednak do zwiększenia plonu wczesnego w porównaniu z formami mineralnymi. Rośliny nawożone chelatami Mn i Cu zawierały z reguły większe ilości tych składników w częściach wskaźnikowych, które analizowano w okresie od maja do sierpnia. Zastosowanie żelaza skompleksowanego chelatami DTPA i EDTA skutkowało zbliżonym plonowaniem pomidora. Użycie Fe-DTPA przyczyniło się do lepszego stanu odżywienia pomidora żelazem, miedzią oraz manganem.

Słowa kluczowe: żelazo, miedź, mangan, chelaty, formy mineralne, plon, stan odżywienia.

## INTRODUCTION

Highly advanced technologies of horticultural crops production involve the application of fertilizers characterized by high phytoavailability of nutrients. Currently, the widespread hydroponic system of tomato and cucumber production involves the use of completely soluble salts used to prepare nutrient solutions. However, ions of metallic microelements, mainly iron and manganese and less so zinc and copper, may quickly change their valence in the presence of oxygen, thus becoming less available to plants (HÖFNER 1992). This phenomenon is frequent in inert media, distinguished by high porosity, excellent aeration and the lack of cation exchange holding capacity. Moreover, the immobilization of metallic micronutrients takes place under the conditions of excessive high pH, surplus of phosphates and carbonates in a growing medium (KOŁOTA et al. 2006).

The application of chelated forms of micronutrients, characterized by good solubility in water and low value of dissociated constant, is crucial for the prevention of immobilization. Chelates make metal cations being gradually released to a medium solution or absorbed by plants in complexed forms (WREESMANN 1996). As proven by KOMOSA et al. (2005), durability and availability of microelements to plants depend on properties of ligands. The most common chelating agents used in fertilizers include EDTA, DTPA and

EDDHA (LUCENA 2003), which differ in strength of chemical bonds of the ion-ligand complex with metals as a function of pH. The shortcoming of these chelating agents, especially EDTA, is their low biodegradability (BOROWIEC et al. 2007, ALBANO 2012). Until today, most of the greenhouse tomato production has been based on open fertigation systems, in which the surplus of nutrient solution from rockwool slabs sinks to the soil and causes the groundwater contamination. Chelating agents can persist in the environment, retaining the capacity to extract and solubilize heavy metals from sediments (ALBANO, MERHAUT 2012).

There are numerous research data indicating high efficiency of plant nutrition with chelated forms of iron (YLIVAINIO et al. 2004, 2006). However, in the case of Cu and Mn, the mineral forms of fertilizers assured higher yields of lettuce grown on peat substrate than EDTA + EDTA chelates of these nutrients (KOZIK et al. 2008a,b). Some differences in yields of this crop were found between the application of Zn chelated and mineral forms (KOZIK et al. 2009). Little information is available on the efficiency of chelate and mineral forms of microelements, especially copper and manganese, in cultivation of tomato on rockwool slabs with nutrient solution continuously supplied to the rhizosphere.

The aim of the present study was to evaluate whether it is necessary to use chelated forms of copper and manganese. Another objective was to assess the suitability of two chelating agents of iron for cultivation of greenhouse tomato on rockwool medium.

## MATERIAL AND METHODS

Two greenhouse experiments with tomato cv. Cunero F<sub>1</sub> were conducted in 2002-2005 at the Horticultural Experimental Station of the Wrocław University of Environmental and Life Sciences.

In the first experiment, established in 2002-2003, the following forms of manganese and copper were evaluated:

- 1) mineral forms of manganese ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) and copper ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ),
- 2) EDTA+DTPA chelate of manganese and mineral copper ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ),
- 3) mineral form of manganese ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) and EDTA+DTPA chelate of copper.

In both years, well-developed transplants were placed on rockwool slabs (100x20x7.5 cm in size; Grodan BV, Master type) in the first third of March. Plants were trained to one stem and tied up with a string as required in the high wire system for a long growing cycle. During the whole growing period, until the end of October, tomato plants were supplied the same nutrient solutions with the following concentration of nutrients (in  $\text{mg dm}^{-3}$ ): N- $\text{NO}_3$ -225, P-6, K-394, Ca-160, Mg-90, Fe-1.40, Mn-0.80, B-0.45, Zn-0.48, Cu-0.08, Mo-0.08, pH 5.50, EC-3.20  $\text{mmhos cm}^{-1}$  (BREŠ et al. 2003). The solutions differed only in forms of manganese and copper.

The second experiment was conducted to evaluate the suitability of DTPA (Librel FeDP7 by Tuhuamij BV) and EDTA (Pionier Fe13 by Interomag Ltd.) as chelating agents for the source of iron in nutrition of tomato plants grown on rockwool. The date of planting, plant management and composition of nutrient solution were similar to those in the first experiment.

Both experiments were established in a randomized block design with 4 replications. A single plot contained 8 plants grown on 2 slabs, in the density of 2.7 plants per m<sup>-2</sup>. Fully ripe tomato fruits were harvested twice a week. The yield was recorded, divided into total and marketable yield of fruits > 3.5 cm in diameter. In addition, early yield, harvested within the first 35 days of yielding, was distinguished. On three occasions during the first experiment, namely in the third decade of June, July and August, and four times during the second experiment, that is at one-month intervals from May to August, samples of index parts of tomato plants were taken for chemical analysis. The index parts of tomato plants were represented by the 8<sup>th</sup> and 9<sup>th</sup> leaves from the plant's top. Fifteen leaves from each plot were collected. The plant material was digested with the microwave method and the content of iron, manganese, copper and zinc were determined by the ASA method. The results were subjected to statistical analysis in a one-factorial design, and the least significant differences were calculated by the Tukey's test at significance level  $\alpha=0.05$ .

## RESULTS

The research results did not prove any significant effect of the examined copper and manganese chelate fertilizers on total yields of tomato fruits. The situation looked different in the case of marketable yields, which appeared to be much lower when copper chelate fertilizer was applied as a source of that nutrient (Table 1). The yields in the remaining fertilization treatments did not significantly differ one from another. The application of Cu and Mn chelate fertilizers had a positive effect on the earliness of tomato fruiting. The early yield from plants fertigated with nutrient solutions containing copper and manganese chelates was considerably higher as compared to that obtained by using mineral forms of these nutrients.

The status of tomato plants' nutrition with iron was not dependent on the application of copper and manganese chelates in the nutrient solution and the mean values were only slightly different, within the range of 112.7-113.4 mg Fe kg<sup>-1</sup>. In June and in August, the iron content in the index parts of tomato plants was similar, being significantly lower in July.

The results shown in Table 2 indicate that manganese used in the nutrient solution as a chelate caused a large increase in the concentration of this microelement in tomato leaves in each term of analysis compared to its

Table 1

The effect of chelates and mineral forms of manganese and copper on yield of greenhouse tomato cultivar Cunero F<sub>1</sub> (kg plant<sup>-1</sup>)

Fertilizer treatments	Yield		
	total	marketable	early
Mn+Cu mineral forms	9.80	8.50	2.75
Mn-chelate + Cu-mineral form	9.98	8.53	2.95
Cu-chelate + Mn-mineral form	9.66	8.11	3.00
Mean	9.81	8.83	2.90
LSD <sub>α=0.05</sub>	n.s.*	0.32	0.11

\*n.s. – differences not significant

Table 2

The effect of chelates and mineral forms of manganese and copper on the content of manganese and iron in index parts of greenhouse tomato cultivar Cunero F<sub>1</sub> (mg kg<sup>-1</sup>)

Fertilizer treatments	Iron				Manganese			
	terms of analysis				terms of analysis			
	June	July	August	mean	June	July	August	mean
Mn+Cu mineral forms	116.9	107.0	116.1	113.3	209.7	198.2	193.2	200.3
Mn-chelate + Cu-mineral form	124.7	97.1	116.2	112.7	235.6	215.9	204.8	218.7
Cu-chelate + Mn-mineral form	114.8	104.4	121.1	113.4	203.1	195.3	196.9	198.4
Mean	118.8	102.8	117.8	113.1	216.1	203.1	198.3	205.8
LSD <sub>α=0.05</sub> for:	term of analysis			1.0				1.7
	forms of microelement			n.s.				1.8
	interaction			2.9				3.5

n.s. – non-significant differences

mineral form. It is worth noticing that in the subsequent terms of analysis, the Mn content in leaves tended to decrease, from 216.1 to 198.3 mg Mn kg<sup>-1</sup>.

On each date of analysis and also as an average value for the whole period of analysis, the copper concentration in the index parts of tomato supplied with Cu-chelate was significantly lower than in the treatment where the mineral form of this nutrient was applied (Table 3). However, the copper chelate improved the uptake of zinc by plants. This effect became distinctly high on the last two dates of sampling, that is in July and August. The manganese chelate did not cause any significant differences in the uptake of zinc compared to its mineral form.

The data from experiment II did not prove any significant influence of the examined fertilizers containing iron complexed by different chelators

Table 3

The effect of chelates and mineral forms of manganese and copper on the content of copper and zinc in index part of greenhouse tomato cultivar Cunero F<sub>1</sub> (mg kg<sup>-1</sup>)

Fertilizer treatments	Iron				Manganese			
	terms of analysis				terms of analysis			
	June	July	August	mean	June	July	August	mean
Mn+Cu mineral forms	9.85	9.65	11.95	10.48	28.95	25.90	24.15	26.33
Mn-chelate + Cu-mineral form	9.40	9.40	11.30	10.03	29.55	26.95	22.80	26.43
Cu-chelate + Mn-mineral form	9.40	8.35	10.05	9.27	29.15	35.45	32.05	32.22
Mean	9.55	9.13	11.10	9.93	29.22	29.43	26.33	28.33
LSD <sub>α-0.05</sub> for:	term of analysis			0.15				0.55
	forms of microelement			0.20				0.60
	interaction			0.30				1.15

n.s. – non-significant differences

(EDTA and DTPA) on tomato total, marketable and early yield of fruits (Table 4).

However, the investigated Fe chelates significantly affected the tomato's nutritional status regarding iron (Table 5). The highest mean iron content in leaves, calculated for the two years of research and four terms of analy-

Table 4

The effect of iron chelates on yield of greenhouse tomato cultivar Cunero F<sub>1</sub> (kg plant<sup>-1</sup>)

Type of chelate	Yield		
	total	marketable	early
DTPA-Fe	9.06	8.67	3.17
EDTA-Fe	9.13	8.73	3.46
Mean	9.10	8.70	3.32
LSD <sub>α-0.05</sub>	n.s.	n.s.	n.s.

ses, was determined in plants fertilized with the DTPA chelate, where it ranged around 149.9 mg Fe kg<sup>-1</sup> d.m. of leaves. A markedly lower mean value of the iron content was found when the element was supplied by the EDTA chelate (141.7 mg Fe kg<sup>-1</sup>). The dynamics of iron uptake and its consequent content in the index parts of tomato were characterized by a high diversity depending on the type of chelate and term of analysis. In the first term of analysis, in May, the mean iron concentration was 152.7 mg Fe kg<sup>-1</sup>,

Table 5

Effect of iron chelates on iron content in the index parts of greenhouse tomato  
(mg Fe kg<sup>-1</sup> d.m.)

Type of chelate	Terms of analysis				Mean
	May	June	July	August	
DTPA-Fe	118.1	140.1	205.3	136.1	149.9
EDTA-Fe	187.2	121.5	118.9	139.3	141.7
Mean	152.7	130.8	162.1	137.7	145.8
LSD <sub>α-0.05</sub> for: term of analysis					2.0
kind of chelates					2.5
interaction					4.3

decreasing to 130.8 mg Fe kg<sup>-1</sup> d.m. on the following term, but peaking in July to its highest level 162.1 mg Fe kg<sup>-1</sup> d.m. In the last term, in August, a significant decrease in the mean value of the iron content was recorded, down to 137.7 mg Fe kg<sup>-1</sup> d.m.

The iron chelates evaluated in the study considerably modified the tomato's nutrition with manganese (Table 6). A higher mean content of manganese (249.9 mg Mn kg<sup>-1</sup> d.m.) was detected in leaves of plants cultivated with the use of DTPA chelating agent, while a significantly lower mean value of this nutrient was determined in plants fertilized with EDTA (237.7 mg Mn kg<sup>-1</sup> d.m.). While analyzing the dynamics of the manganese uptake through the plant growing period, it can be noticed that from May to June its content in leaves rapidly increased, on average from 135.6 to 285.9 mg Mn kg<sup>-1</sup> d.m. and maintained on the level of 242.0 and 311.8 mg Mn kg<sup>-1</sup> d.m. in July and August, respectively.

Table 6

Effect of iron chelates on the manganese content in the index parts of greenhouse tomato  
(mg Mn kg<sup>-1</sup> d.m.)

Type of chelate	Terms of analysis				Mean
	May	June	July	August	
DTPA-Fe	146.1	270.2	244.5	338.9	249.9
EDTA-Fe	125.1	301.5	239.4	284.6	237.7
Mean	135.6	285.9	242.0	311.8	243.8
LSD <sub>α-0.05</sub> for: term of analysis					2.8
kind of chelates					3.2
interaction					5.6





Table 8

Effect of iron chelates on the zinc content in the index parts of greenhouse tomato  
(mg Zn kg<sup>-1</sup> d.m.)

Type of chelate	Terms of analysis				Mean
	May	June	July	August	
DTPA-Fe	36.6	38.7	35.4	35.0	36.4
EDTA-Fe	33.3	53.7	48.3	49.9	46.3
Mean	35.0	46.2	41.9	42.5	41.4
LSD <sub>α=0.05</sub> for: term of analysis					0.5
kind of chelates					0.6
interaction					1.1

## DISCUSSION

Yields of tomato Cunero F<sub>1</sub> cultivar obtained in our greenhouse experiments were quite similar to the ones reported from other trials (NURZYŃSKI 2004, 2006, PAWLIŃSKA, KOMOSA 2004, JAROSZ, DZIDA 2011). The application of mineral forms of Mn and Cu appeared to be as efficient as the use of DTPA chelates of these nutrients with respect to the total yield of fruits. However, the Cu chelate was less effective in stimulating marketable yield, while both tested chelates caused accelerated maturation of fruits and consequently higher early yields of tomatoes. In a trial conducted by KOZIK et al. (2012), the yield of greenhouse lettuce grown on peat substrate was unaffected by the source of micronutrients applied in lower doses, but mineral forms of Mn, Cu and Zn produced better effects than their EDTA and DTPA chelates when supplied in higher amounts to a growing medium. The good results achieved by mineral forms of micronutrients in a nutrient solution may be attributed to creating favorable conditions for their uptake and preventing immobilization. Likewise, in an experiment conducted by KOMOSA et al. (2002), the source of Fe in a nutrient solution did not affect the yield of tomato fruits. No differences in the growth and final weight of marigold biomass supplied with Fe-EDTA and Fe-DTPA sources of this nutrient were observed by ALBANO and MERHAUT (2012).

The iron content in plants is generally between 50 and 200 Fe kg<sup>-1</sup> d.m. (SONNEVELD, VOOGT 1985), and the recommended level for tomatoes should exceed 60.0 mg Fe kg<sup>-1</sup> d.m. of leaves. The amounts of Fe in our study, which varied from 97.1 to the maximum 205.3 mg Fe kg<sup>-1</sup> d.m., justify the conclusion that irrespective of the type of iron chelate and source of Mn and Cu in a nutrient solution all tomato plants were properly fed with this nutrient. Similar levels of iron in the tomato's index part were

obtained by CHOJURA and KOMOSA (2003) KOMOSA et al. (2002), and DYŠKO et al. (2009).

Numerous research data have proven that both deficiency and excess of manganese can be harmful to tomatoes (SHENKER et al. 2004). SERESINHE (1996) reported that an optimum manganese content in fully developed tomato leaves ranges from 50 to 500 mg Mn kg<sup>-1</sup> d.m. Even a wider range of its content, within 25-1000 mg Mn kg<sup>-1</sup> d.m., was proposed by HORST (1988). SHENKER et al. (2004) determined that at a concentration of 16.8 mg Mn kg<sup>-1</sup> d.m, the chlorophyll content in tomato leaves was not markedly lower than at 207.4 mg Mn kg<sup>-1</sup> d.m. which appeared to be phytotoxic. LE BOT et al. (1990b) reported that 250 mg Mn kg<sup>-1</sup> d.m is the upper safe limit for the manganese content in tomato leaves. Other researchers have pointed out that the toxic effect of this component can be reduced by maintaining an appropriate manganese: magnesium ratio (HORST 1988, LE BOT et al. 1990a). In our trials, the amounts of this element were within 193.2-235.6 mg Mn kg<sup>-1</sup> d.m. in experiment I and 125.1 - 338.9 mg Mn kg<sup>-1</sup>d.m. in experiment II. The data indicate a good supply of the tomato plants with Mn, irrespective of the source of this nutrient and type of Fe chelating agent. A similar level of Mn was also determined by CHOJURA and KOMOSA (2003). High quantities of manganese usually induce a reduced uptake of iron, because these two ions compete for proteins transporting them through the plasma membrane (KORSHUNOVA et al. 1999, GUNES et al. 1998). Such relationships have become apparent in our research, namely an increase in the manganese content in tomato leaves was usually accompanied by a decrease in the iron concentration.

The copper content in the tomato's index parts was less varied than that of the remaining microelements. In the first experiment, the content of this nutrients did not exceed the range of 8.35-11.95 mg Cu kg<sup>-1</sup> d.m., with the mean value for all analyses determined at 9.93 mg Cu kg<sup>-1</sup> d.m. In the second experiment, the mean concentration of copper in tomato leaves equaled 9.30 mg Cu kg<sup>-1</sup> d.m., and the results of analyses in particular terms were between 8.25 and 10.78 mg Cu kg<sup>-1</sup> d.m. Such small variation could be have been caused by the retention of copper ions in root tissues. CHAIGNON et al. (2002) concluded that when this is the case, less copper is transported through the xylem so that the variation in the copper content in leaves is much smaller. The mean copper content determined in our research was similar to the data presented by CHOJURA and KOMOSA (2003), while being higher than reported by GINOCCHIO et al. (2002), who assumed that an optimum level of this nutrient is above 4.0 Cu kg<sup>-1</sup> d.m. of tomato leaves.

The mean content of zinc, ranging around 28.3 mg Zn kg<sup>-1</sup> d.m in the first experiment and 41.4 mg Zn kg<sup>-1</sup> d.m in the second one, was on a level of optimal tomato nutrition determined by GUNES et al. (1998). The same authors claimed that the zinc content in tomato leaves may be found within

a wide range from 25 to 250 Zn kg<sup>-1</sup> d.m. KAYA and HIGGS (2001) report that a minimum content of this component for tomato equals 25 Zn kg<sup>-1</sup> d.m. KAYA and HIGGS (2002) recorded visible symptoms of zinc deficiency such as curled leaves and shortened internodes at the concentration of 23.0 Zn kg<sup>-1</sup> d.m. In our first experiment, the Zn content was in the range of 22.8-35.45 Zn kg<sup>-1</sup> d.m. Those values were close to the lower limit, but no symptoms of ill health of plant could be observed. In the second experiment, the range of zinc content in leaves was considerably wider: from 33.3 to 53.7 Zn kg<sup>-1</sup> d.m. A similar content of zinc in index parts was determined by CHOJURA and KOMOSA (2003). Higher quantities of this element in leaves of tomato cultivated in rockwool were reported by PAWLIŃSKA and KOMOSA (2002, 2004).

Recapitulating, with the output from our experiments, we can conclude that the use of Mn chelate brought about better results while Cu-chelate had an adverse effect on the uptake of these nutrients by greenhouse tomato in rockwool cultivation compared to mineral forms of manganese and copper. The only beneficial impact of these forms of Mn and Cu was a bigger early yield of fruits. In an assessment of different aspects of using Mn and Cu chelates in practice it is also necessary to consider that they are more expensive than mineral forms.

## CONCLUSIONS

1. The application of chelate forms of copper and manganese did not influence the total yield of tomato fruits, but it contributed to considerable increase in a very early yield if compared to mineral forms of these nutrients.

2. Manganese used as a chelate and copper in the mineral form significantly improved the nutritional status of plants by Mn and Cu, respectively.

3. The application of iron complexed with different chelating agents did not cause any significant variation in tomato marketable as well as early yield of fruits.

4. The use of DTPA as an Fe source contributed to a better status of tomato nutrition with iron, manganese and copper relative to the use of EDTA Fe.

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