STUDY ON THE CHANGABLE, UNCHANGABLE AND ORGANIC ZN CONTENT FROM THE SOIL

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The Zn ion is part of 70 metal-enzymes, it actions as an activator for some enzymes having a physiological role and it also has a tempering role in the polypeptide action. The Zn is at the same time an essential component in establishing the cytoplasm ribosome. The Zn activates the tryptophan synthesis which is an intermediary product for obtaining the auxin (the β-indoleacetic acid). The Zn is involved in the nitrates reduction; in case of Zn deficiency the ribonuclease activity is diminished, it accumulates in nitrates plants, amides, organic acids that cannot be oxidized through the breathing system. The zinc deficiency affects the plants and it can be seen especially in fruit trees, corn, beans, and potatoes. A study on zinc concentrations is required for the above mentioned cultures, especially in the areas where agriculture is an important economical branch.

The technique of speciation in the soil treatment was applied in order to monitor the zinc possible manifestations in the soil. After that the spectrophotometric method was applied with the purpose of dosing the changeable, unchangeable, organic Zn content from the soil.

The present study was performed on garden soil from Galati County, the Covurlui valley. It was discovered that the zinc from the soil can be found in the 3-22ppm domain. The acid, neutral or basic character is tightly connected to the changeable Zn. The zinc in the soil can be found in small quantity under 1 ppm and it is represented by the zinc salts (ZnS, $ZnCO_3$) which are soluble in an acid environment. The analyzed soil has the pH 7-7,4. The changeable zinc has a 5,12-6,45 ppm concentration. The unchangeable zinc has a 9 ppm concentration. In the organic part of the soil, the zinc found as metal-complexes being in 8,6 ppm concentration. The retention of Zn under unchangeable form in clay, with a neutral pH related to the chelate groups and complexes with the organic matter which can be a cause for the plants zinc deficiency.

***Key words**: sequential extraction, technique of speciation, soil, zinc*

The Zn element can be found as a silicate component of the soil in clay-bearing minerals, oxides, hydroxides and within the organic matter.

The Zn forms soluble salts with more anions. The more acid the pH is, the more increases the concentration of the soluble forms in the soil solution [3].

The total Zn content in the lithosphere varies between 10 and 300 ppm. The soils formed on basic rocks have a higher Zn content than those formed on acid

rocks and on the surface horizon the total Zn is in average between 24 and 110 ppm. The podzolic soils and the soils having a sandy texture have a lower Zn content [4].

The Zn content in plants is the tenth-order from a percent.

The physiologic role of Zn was rendered evident by Freytag (1868) and later by Jensch (1894), Javillier (1907), Bertrand (1931) [1].

The Zn is a constituent of over 70 metalloenzymes from the dehydrogenases, peptidases and proteases group, such as: aldolase, carbohydrose, alcoholic dehydrogenase, glutamic dehydrogenase. The Zn is an activator for other enzymes such as enolase, dipeptidase and it has the role of tempering the polypetidase action.

One of the most important functions attributed to the zinc element is that of activating the tryptophan synthesis which is an intermediary product of auxin (β-indoleacetic acid).

In case of Zn deficiency the ribuloso-1.5-difosphate-carboxylase activity decreases with 40-90%, which leads to a decrease in CO_2 fixing in the photosynthesis process.

The Zinc is capable to bind to NAD and respectively to NADH forming an enzymatic complex. It has catalytic and stability characteristics concerning the proteic part of the enzyme.[2].

At the same time the Zinc plays an important part in synthesis of the stain case of Zinc deficiency the starch synthesis is interrupted, ARN decreases and as a consequence the proteins appear.

The Zinc is involved in the nitrates reduction; in case of Zinc deficiency the ribonuclease activity decreases and there is an accumulation of nitrates, amides (asparagine, glutamine), organic acids (citric, fumaric) in the plant which cannot be oxydated through the respiratory chain. [9].

The Zinc deficiency leads to the appearance of red spots at the level of the leaves.

At first the Zinc insufficiency leads to the sudden decrease of the ARN level in the cell ribosomes due to the inactivation of some enzymes.

The decrease of the β-indoleacetic concentration whose synthesis is activated by Zinc (tryptophan synthase), causes morphological deformations in the plants growing points, the internodes shortening and the appearance of plants under the form of bushes or rosette. The deficiency can be found especially in fruit trees, corn, beans, and potato [2].

The zinc excess is rarely met especially in the areas affected by heavy metals pollution (Pb, Cd, Zn, Cu) and acid soils (pH<5.8 – 6.0) because the advanced acidity conducive of bio-accessibility. Under the circumstances the soluble Zn content in the soils decreases the value 100-150 ppm [6].

In the present paper the sequential extraction was applied as a method of soil processing in order to dose selectively the Zn microelement. The spectophotometric analyzing method was used for dosing and the Zn fractions from soil were rendered evident: accessible to the plants under the form of oxides from

the organic matter and under the form of complex combinations. A physical-chemical characterization of the analyzed soil was made at the same time.

MATERIAL AND METHOD

The multi-parameter, Consort C862, Belgium was used for the physical-chemical characterization of the soil extract and the spectrophotometer Spectrquant Nova 60, Merck Germany was used in order to dose the Zinc.

All reagents used had analytical purity (ap).

The soil samples' processing was performed using the sequential extraction method in three stages [15].

The procedure presupposes the exposure of a solid sample (soil or sediment) to successive reagents attacks having different chemical properties (acidity, reduction potential or complex properties) to obtain extracts containing the ions of the respective metal in different oxidation states [12]. The analyses were performed three times, the results being the arithmetic average for at least three determinations. All calculations and the statistic determination were realized with the program Excel from Windows XP.

RESULTS AND DISCUSSIONS

By treating the soil samples with acetic acid of concentration 0.11 mol L^{-1} for a pH=2.85 the soluble and changeable ions in the metals found in the soil are extracted.

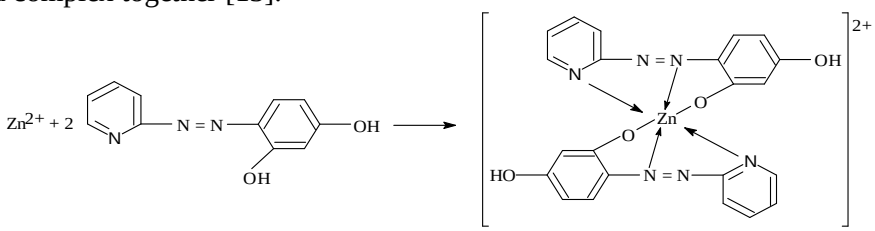
The metals present in oxides are obtained by adding hydroxylamine chlorinate 0.1 mol/L over the residuum from extract I, for a pH=2.

Extract III is obtained by treating the residuum from extract II with peroxide for a pH=2. The metals connected to the organic matter and the sulphides are extracted from extract III.

The residuum left after the last extraction is treated with aqua regia in order to extract the insoluble metals in the subsequent stages.

The extracts from each stage evaporate almost to dry on water bath. 5 mL HNO_3 of concentration 1 mol L^{-1} is added in each extract. The extracts are brought to quote balloons of 50 mL and are brought up to the sign with bi-distilled water.

For quantification the Zn^{2+} ions from the four extracts are determined with the Merck Test based on the reaction with the pyridylazoresorcinol (PAR) forming a red complex together [13]:



The samples treated according to the reaction were subjected to spectrophotometry *(tab. 1)*.

Table 1

The values of the Zn^{2+} ions concentration read directly from the spectrophometer

Extract	Zn^{2+} ions concentration (mg/L)
Extract I	0.205
Extract II	0,363
Extract III	0,344
Extract IV	0,321

The mathematical processing of the data obtained at the samples spectrophotometry and reporting to the soil quantity subject to analyze leads to finding the concentration of the species containing Zinc in the four extracts obtained by soil processing through the speciation method. The results obtained are graphically presented *(fig. 1)*.

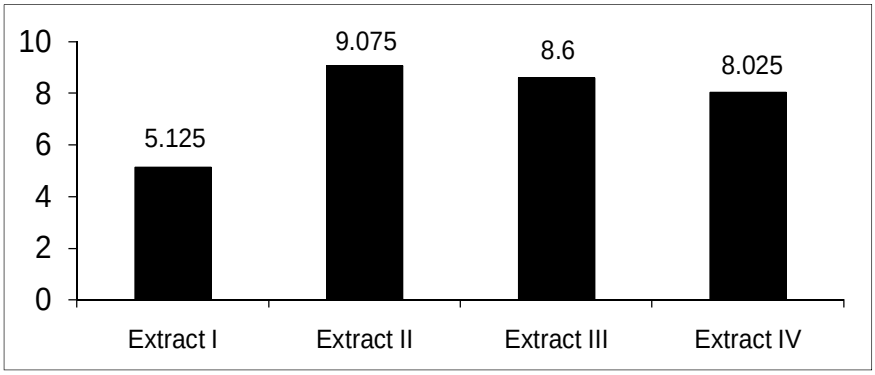


Figure 1 **Graphic representation of the Zn^{2+}(ppm) ions concentrations from the soil extracts**

The Zinc from extract I represents the soluble Zinc, which due to the soil neutral pH is in a small quantity, respectively 5.125 ppm. The Zinc from extract I is under the form of neutral carbonate and basic carbonate which once treated with acetic acid is extracted under the form of acetate freeing the carbon-dioxide [5]. The Zinc solubility from the soil reaches a maximum at pH 4 and a minimum under conditions of neutral or basic pH with each extra pH unit the solubility decreases 100 times [7].

The highest quantity of Zinc 9.075 ppm is found in extract II representing Zinc under the form of oxides.

At the same time, a significant Zinc quantity was extracted from the soil organic matter 8.6 ppm, between the limits framed by the specialized literature 3 - 22 ppm [8].

In residuum, the Zinc quantity 8.025 ppm, is extracted from the Zinc combinations, insoluble in the extractable reagents used in stages I-III, unavailable combinations for plants [11].

For a correct interpretation of the results obtained, analyses were performed in order to obtain some information about the physical-chemical properties of the soil (*tab. 2*).

Table 2

Values of some physical-chemical parameters for the analyzed soil

Moisture (%)	15.23
Conductivity (µs/cm)	255
pH	7.91
Redox Potential (mV)	- 53.8
Ca^{2+} (mg/100g soil)	33.4
Mg^{2+} (mg/100g soil)	145.92

The soil humidity of 15.2 3% is acceptable as being enough to keep an optimum content of diluted salts in the soil solution.

From the values obtained for conductivity results that the analyzed soil is rich in mineral salts diluted in the soil solution. Aside from microelements, the plants also consume macro-elements such as: calcium, magnesium, nitrogen, phosphorus, sodium, potassium necessary for growth and the normal biological cycle. From the analyses performed it can be noticed that the soil has a high content of Mg^{2+} ions. The magnesium is part of the chlorophyll structure and plays a vital part for the plants. The concentration of Ca^{2+} ions is within acceptable limits. [10]. An increase in Ca^{2+} concentration reduces the zinc absorption by the plants leading to unwanted phenomena in the biological processes [14].

The values of the redox potential indicate a soil having a weak reducing character which presupposes a light anaerobiosis. This property is favorable for maintaining the ions for some microelements in inferior oxidation states, accessible to plants. But the Zinc absorption is highly reduced under anaerobiosis conditions, and for this reason it is compulsory for the soil to be worked on for aeration purposes.

CONCLUSIONS

The sequential extraction method allows for the correct evaluation of the content in microelements on fractions types and oxidation states.

The Zn^{2+} extractable fraction represents 16.62 % from the total zinc from the soil, being enough for the harmonious development of plants.

Extract II emphasizes that the analyzed soil contains Zinc under the form of oxides, in quantity of 9.075 ppm, representing 29.44 % from the total zinc.

From extract III results that the Zn^{2+} ions can be found either under the form of sulphides or in organic substances, in quantity of 8.6 ppm, that is 27.89 % from the total zinc.

Important information were obtained from the study of some physical-chemical properties of the analyzed soil regarding conductivity, the total salt content, the soil reaction and the redox potential.

The analyzed soil has a neutral reaction towards weak basic which determines keeping the microelements in soil under the deposit form.

From the values of the redox potential results the fact that the soil presents anaorobiosis conditions where the reduction processes can be favoured. These conditions are favourable for maintaining a fraction equilibrium where the studied microelement is found.

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