

# Study on Iron and Manganese from Soil by Elemental Speciation

MARIA CIOROI\*

University "Dunarea de Jos" of Galați, 47 Domneasca Str., 800008, Galati, Romania

*Elemental speciation has become an important issue in different fields of chemistry science. Research interests have moved from total element composition of the sample towards determination of species that are responsible for the biochemical and geochemical behaviour of elements. In this report, the determination of total element concentrations has been done for Fe, Mn, as essential elements with specific biological function and the determination of each soluble species of Fe(3+), Mn(2+), from soil solution and adsorptive forms on organic - mineral soil complex. The total content of analyzed microelements was as following: iron - 1058 ppm and manganese was - 430 ppm. Speciation analysis is used for the separation and quantification of different oxidation states or chemical forms of a particular element. The quantity of above soluble species in adsorptive complex or soil solution is as following: iron (3+) around - 10 ppm and manganese (2+) is - 90 ppm. The quantification of the available soluble forms of microelements is important for the soils supply with necessary nutrients in growing of plants.*

*Keywords: elemental speciation, iron, manganese, soil*

The microelements occurring in plants are provided from soil where they are present in four forms: soil minerals, organic metal chelates, adsorbed nutrients and dissolved ions. Together, these four sources perform two functions: to store nutrients and to make nutrients available to plants. A chemical analyze of soil helps us to appreciate the state of elements distribution.

Depending on their origin, trace elements exist in different mineral forms and chemical compounds, in different combinations with mineral and organic components of soil and sediments which may vary in concentration according to various conditions: pH, redox conditions, temperature, the presence of organic matter, and microbiological activity. All these factors strongly influence the biogeochemical cycles of elements in environment [2].

The micronutrients, which are needed for plants only in trace amounts (< 0.01% on dried material), are iron (Fe), manganese (Mn), boron (B), zinc (Zn), copper (Cu), molybdenum (Mo)[6].

They especially have an essential role in the vital cycle of plants and also an enzymatic and catalytic effect in vegetal metabolism [9].

From the above elements, iron and manganese have an important role in plants growing [12].

Iron Fe<sup>2+</sup> and Fe<sup>3+</sup> promote formation of chlorophyll implied in fixing of atmospheric N<sub>2</sub>, in synthesis of proteins. Iron is implied on enzyme mechanism which operates in the respiratory system of cells and catalyses reactions involving cell division and growth [3].

Manganese Mn<sup>2+</sup> is predominant in metabolism of organic acids, it activates the reduction of nitrite and hydroxylamine to ammonia, it has a role in important enzymes involved in respiration and enzyme synthesis, it is an activator of enzyme reactions such as oxidation/reduction, hydrolysis and directly influence sunlight conversion in the chloroplasts [8].

Since the behaviour of the elements in the soil-water-plant system depends on their forms, the determination of metal traces in soil is often performed by single or sequential extraction [15]. The procedures involve

subjecting a solid sample (soil or sediment) to successive attacks with reagents possessing different chemical properties (acidity, redox potential, or complexing properties) in which each extract includes a part of the metals trace associated with the sample.

The determination of total metal content only is not an indicator of the mobility or bioavailability of metals in soil. Chemical speciation can be defined as the process of determining and identifying specific chemical species or binding forms; it allows one to determine the availability and mobility of the metals in order to understand their chemical behaviour.

In this study, a sequential extraction was performed according to the procedure recommended by the Standards, Measurements and Testing Programme of the European Union for the determination of iron and manganese [13].

## Experimental part

### Materials and methods

#### Instrumentation

Metal determinations in the soil extracts and digests were carried out by means of a Perkin Elmer Model 3110 flame atomic absorption spectrometer, with an air-acetylene flame. A centrifuge (Hettich Rotofix 32, Germany) for complete separation of the extracts from the residues, a multiparameter Consort model C 863T (pH; conductivity) with resolution of 0.001pH and 0.001μS/cm, and magnetic stirrer „Agimatic-N”, with electrical heater were used throughout all the experiments.

#### Reagents

Analytical reagent grade chemicals and double-distilled water were used for preparing all solutions.

Stock solutions containing 1000 mg L<sup>-1</sup> of the analytes were prepared from nitrate salts of Fe, Mn, in HNO<sub>3</sub> of 1%. Working standard solutions were prepared in 1 mol L<sup>-1</sup> HNO<sub>3</sub> by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents in equal quantities as described in the analysis procedure throughout the experiments.

\* email: Maria.CIOROI@ugal.ro

**Table 1**  
FOUR-STAGE SEQUENTIAL EXTRACTION SCHEME

Extraction step	Reactive / concentration / pH	Solid phase
1	Acetic acid: CH <sub>3</sub> COOH (0.11 mol L <sup>-1</sup> ), pH 2.85	Exchangeable, water and acid soluble (e.g., carbonates)
2	Hydroxylammonium chloride: NH <sub>2</sub> OH HCl (0.1 mol L <sup>-1</sup> ) at pH 2	Reducible (e.g., iron/manganese oxides)
3	Hydrogen peroxide: H <sub>2</sub> O <sub>2</sub> (8.8 mol L <sup>-1</sup> ), followed by ammonium acetate: CH <sub>3</sub> COONH <sub>4</sub> (1.0 mol L <sup>-1</sup> ) at pH 2	Oxidisable (e.g., organic substance and sulphides)
4	Aqua regia: 3HCl + HNO <sub>3</sub>	(Residual) <sup>a</sup> , Remaining, non-silicate bound metals

### Sample collection and pre-treatment

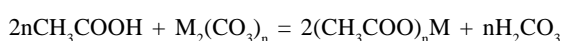
Soil samples from vegetables garden were collected in polyethylene bags. The samples were collected from the top 5-cm and 30-cm layer of the sampling with a stainless-steel spoon. It was applied the method of samples collection from isolated points [10]. The collected soil was uniformly distributed on a platform. Then the points from where the soil samples were collected have been established. Samples were immediately taken to the laboratory and then stones and plant fragments were removed by passing the sample through a 2-mm sieve. Afterwards, the samples were dried at 105 °C in an oven; then the dried samples were crushed to a fine powder using a mortar and passed through a 200-mesh sieve. They were homogenized and stored in polyethylene bags until the analysis.

### Extraction procedure

The sequential extraction procedure is given in table 1.

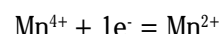
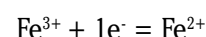
### Exchangeable metals

The soluble metals were extracted by adding acetic acid. The procedure is described in detail on [15]. Acetic acid 0.11 mol/L reacts on metallic carbonats resulting metallic ions as acetat salts after general reaction:



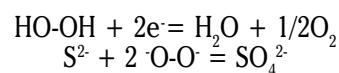
### Metals bound to iron and manganese oxides

Metals bound to iron and manganese oxides were extracted by adding hydroxylammonium chloride (adjusted to pH 2 with 2 mol L<sup>-1</sup> nitric acid) onto the residue from the first step [15]. The role of hydroxylammonium chloride as reducer reagent is to transform the iron and manganese from the superior oxidation state to the inferior oxidation state:



### Metals bound to organic matter and sulphides

Hydrogen peroxide was carefully added in small aliquots to the residue from the second step. Hydrogen peroxide play an oxidant role in redox processes and oxidizes metal sulfides to sulfates:



### Residual

The analysis of the residue was performed using aqua regia for metals insoluble in the previous steps [5].

The extracts acquired after each sequential extraction stage were evaporated to near dryness. Each extract was completed to 5 mL with 1 mol L<sup>-1</sup> HNO<sub>3</sub>.

## Results and Discussion

The concept of soil fertility includes not only the quantity of nutrients a soil contains but how well they are protected from leaching, their availability, and other chemical characteristics [7].

The determinations of Fe, Mn in the extracts were performed by flame atomic absorption spectroscopy (FAAS).

From the results obtained by flame atomic absorption spectroscopy of soil samples will be presented now only two elements, iron and manganese, since these have an important role on plants growing. Some parameters, as conductivity, pH-values and nitrate anion concentration of soil samples are presented in table 2.

**Table 2**  
SOIL CHARACTERISTICS

Sample	pH	Conductivity microS/cm(20°C)	NO <sub>3</sub> <sup>-</sup> (ppm)
5 cm	8,2	163,2	21
30 cm	7,87	155,1	28,6

**Table 3**  
CONCENTRATION OF ANALYZED ELEMENTS, ppm

Element	Depth of soil sampling	Fraction 1	Fraction 2	Fraction 3	Residual
		(Fr.1)	(Fr.2)	(Fr.3)	
		1	2	3	4
Fe(III)	5 cm	9,84	150	230	687
	30 cm	10,5	160	220	662
Mn(II)	5 cm	81	110	83	142
	30 cm	90	120	81	145

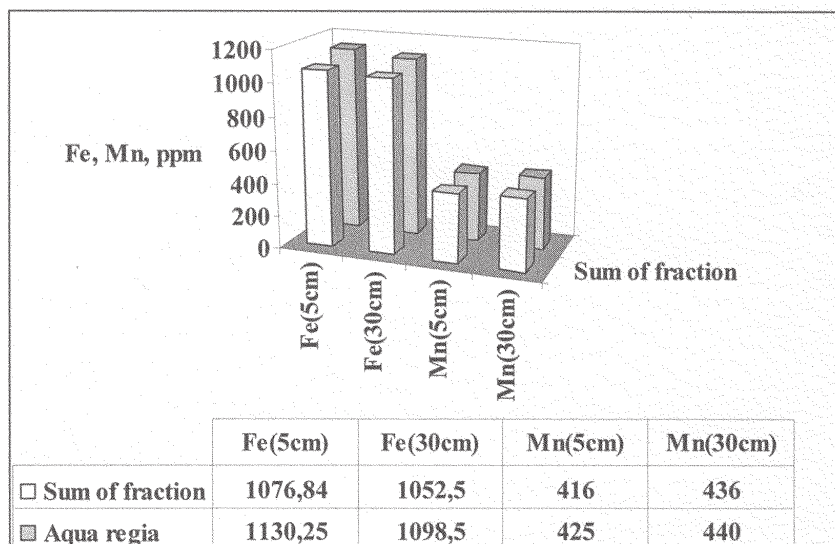


Fig. 1. Total concentration of Fe and Mn: white bars – sum of the four extraction stages; green bars – treatment of soil samples with aqua regia

Among the different factors affecting the availability of microelements, soil solution pH is the major one. The analyzed soil samples have a neutral to slightly alkaline character (pH is  $7.87 \div 8.20$ ). In these conditions we expected that the concentration of soluble forms of micronutrients to be lower than the concentration of microelements in slightly acidic medium.

The concentration of soluble iron from fraction 1 is: 9.84 ppm at 5 cm and 10.5 ppm at 30 cm soil layer depth. The concentration of exchangeable manganese ions from fraction 1 represents just 20% of total manganese while the soluble iron is only about 1% of total iron from analyzed soil (table 3).

The concentration of  $\text{NO}_3^-$  gives information about the presence of nitrates in soil. The correlation between pH and the concentration of nitrate ion allows us to conclude that the soil has neutral nitrates but not so much iron and manganese nitrates. The nitrates of transitional metals have a slightly acidic character. Most probably iron and manganese from fraction 1 are found in carbonates, soluble in  $\text{CH}_3\text{COOH}$ .

The distribution of micronutrients in the sample allows us to predict their mobility and bioavailability. Iron and manganese contents (ppm) for each extraction and residual steps, determined by the sequential extraction method, are illustrated in table 3.

The iron from Fr.1 is about 0.9 ÷ 1% of total iron extent in analyzed soil. Concentration of iron in Fr. 2 is fifteen times bigger than the iron concentration of Fr. 1. This fact shows us the presence in soil of iron with a superior oxidative state (+3) in oxides like as  $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ . In Fr.3 the concentration of iron is 230 ppm at 5 cm and 220 ppm at 30 cm soil layer depth. This result means that a great quantity of iron is retained in soil by the organic matter and sulphides [14]. The highest Fe content was approximately 64% in the residual fraction. This result indicates a high quantity of iron in soil but it is not accessible for plants.

The exchangeable form of manganese from Fr. 1 is 80 ÷ 90 ppm, these being the normal limits for chemical composition of soil [11]. The reduced form of manganese was extracted by hydroxyl ammonium chloride and represents 110 ppm at 5 cm and 120 ppm at 30 cm soil layer depth. That represents a stable form of manganese on oxidative state (4+), like  $\text{MnO}_2$  or other insoluble compounds of manganese(IV). This quantity of manganese could be considerate a good source which could be transformed in soluble form by adequate procedures if necessary. The concentration of manganese

in soil is partitioned as following: 66% in extractible and reducible phase, 33% in residual fraction.

The total contents of metals obtained by direct dissolution of the soil samples using aqua regia were compared with the sum of metal contents obtained from each fraction of the sequential extraction procedure and residue analysis (fig. 1) The results from direct dissolution of the soil samples using aqua regia are in good agreement with the conclusions obtained with the total metal levels based on the sum of sequential extraction and the residual steps.

The obtained results were comparable, the coefficient of correlation was 0.9887 and coefficient of variation for each set of measurement was for iron and manganese under 6% and 0.8% respectively.

## Conclusions

In this work has been done the determination of each soluble species of iron and manganese from soil solution and adsorptive forms on organic - mineral soil complex.

For the separation of different oxidation states of elements was used speciation analysis. The soil reaction (pH), conductivity and content of nitrate ions were determined since they are important factors for the availability of microelements in soil.

The obtained results show a good correlation between soil pH and analyzed nutrients. The slightly alkaline character of soil keeps the iron and manganese in high oxidation state which will represent a good natural source of these nutrients. An important aspect is to monitor from time to time the pH of soil and to adjust it until slightly acidic character.

The  $\text{NO}_3^-$  concentration from analyzed soil samples indicates that the soil is poor in transitional metals nitrates. The neutral to slightly alkaline character of soil suggests us that the  $\text{NO}_3^-$  is bounded by alkaline metals to form neutral nitrates.

The exchangeable iron (+2) occurs in a small quantity since analyzed soil is well aerated. However the values range (9.84 – 10.5 ppm) is enough for plants growing [5]. The concentration of manganese in residual form is approximately 34%; the rest of 66% represents the three forms: extractible, bounded of oxides and organic substances. The extractible form of Mn is in average 20.14 ppm, which means a good source for plants and vegetables.

The composition of analyzed soil samples is in good agreement with the typical soil metal contents [1].

Some elements play a double role – they are essential for leaving organisms in a limited concentration and above it they become toxic. The toxicity of metals depends on their chemical forms and in such cases the speciation analysis should be used [4].

Therefore speciation analysis is very important to separate and to identify specific or binding forms of metals and allows to assess the availability and mobility of metals in order to understand their chemical behavior.

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